EFFECTS OF EXPERIMENTAL SCALE ON THE ADSORPTION OF TWO PHARMACEUTICALS DETECTED IN MUNICIPAL WASTEWATER EFFLUENT

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ABSTRACT

Effects Of Experimental Scale on the Adsorption of Two Pharmaceutical Drugs Detected in Municipal Wastewater Effluent

Michael Thomas Moore

Pharmaceutical drugs are being produced and consumed in increasing quantities every year and are poorly treated by conventional wastewater treatment processes, leading to increasing detection of such compounds in surface water, groundwater, and municipal drinking water. Soil aquifer treatment (SAT) is a promising method for treating these emerging compounds through combined adsorption and degradation of target compounds in soil. This thesis examines the consistency of results from typical studies like adsorption isotherms and soil columns utilized in analysis of SAT performance, across varying experimental scales.

The adsorption behavior of two pharmaceuticals was investigated as a function of experimental scale and soil organic content in adsorbent media. This thesis shows that broad trends in pharmaceutical adsorption are not dependent upon experimental scale. Across adsorption isotherm, bench-scale soil column, and large-scale soil column experiments, adsorption and of both drugs was greater in organic soil than inorganic soil, although dispersive transport may have increased in some experiments. Across all experiments, carbamazepine was adsorbed by soils more than diclofenac. Some inconsistencies were observed across scales between the two organic soils, a medium-organic and high-organic soil, where adsorption was generally greater in high organic soil, but sometimes observed to be greater in medium organic soil. This may suggest that the decrease of experimental control resulting from increased experimental scale obfuscates more nuanced relationships in SAT experimental conditions. Broad trends in data showing whether or not a soil displayed significant adsorptive behavior and which pharmaceutical was adsorbed more were consistent. However, the degree of partitioning via adsorption varied across scales as experimental control decreased with increasing physical scale.

Keywords**:** Adsorption**,** Carbamazepine, Diclofenac, Experimental Scale, Isotherms, Soil Aquifer Treatment, Soil Columns

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Despite the irregularities of my first year at Cal Poly as a graduate student, I have learned an immense amount about civil and environmental engineering and even some other related fields. A thesis is supposed to be a culminating experience, and my thesis is certainly no exception. Through this paper there are clear links to essentially every class I’ve taken in my time at Cal Poly. I want to thank the members of my committee especially. Dr. Manheim challenged me like few other professors have, and gave me great opportunity to directly tie in my undergraduate background in hydrogeology with engineering approaches, and made me get very comfortable working with groundwater modeling. I’m also grateful for the opportunity to have worked as a grader under Dr. Manheim, where I got a taste for all the time my professors have spent grading our assignments. Dr. El Badawy opened my eyes to a whole field I had no idea existed with environmental nanotechnology and evoked that sense of wonder I felt in science classes as a kid when the teacher would do a cool experiment, but this time we were the ones doing cool experiments.

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I’m very proud of the body of work presented here, and hope that the countless people who helped me accomplish share that pride as well.

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ABBREVIATIONS

ASTM – American Society for Testing and Materials

CBZ – Carbamazepine

DCF – Diclofenac

DI – Deionized

DF – Detection Frequency

DR – Detection Ratio

DWTP – Drinking Water Treatment Plant

EBCT – Empty Bed Contact Time

EC – Emerging Contaminants

EH&S – Environmental Health and Safety

EPA – Environmental Protection Agency

HPLC – High-Performance Liquid Chromatograph

IPR – Indirect Potable Reuse

K_{OW} – Octanol Water Partition Coefficient

K_{OC} – Organic Carbon Distribution Coefficient

MDL – Method Detection Limit

PFAS – Poly or Per-fluoroalkyl Substances

PPCPs – Pharmaceuticals and Personal Care Products

PTFE - Polytetrafluoroethylene

PV – Pore Volume

RMSE – Root Mean Square Error

SAT – Soil Aquifer Treatment

SOC – Soil Organic Carbon

TCE – Trichlorethylenes

USGS – United States Geological Survey

WWTP – Wastewater Treatment Plant

1. INTRODUCTION

This study focuses on the adsorption of two pharmaceutical drugs commonly detected in treated wastewater effluent and sometimes detected in drinking water: diclofenac and carbamazepine. Pharmaceuticals and personal care products (PPCPs) have been detected with increasing frequency in municipal wastewater both before and after treatment at conventional wastewater treatment plants (WWTPs) (Jurado et al. 2014). Most WWTPs (Kwon and Rodriguez 2014) are very effective at treating and removing contaminants which were understood, regulated, and well characterized at the time of their construction. PPCPs however fall into the broad class of emerging contaminants (ECs) which have only recently started to be characterized and treated. Figure 1 shows a conceptual model of PPCP pathways in the environment, where humans and livestock consume PPCPs then they enter the environment and circulate.

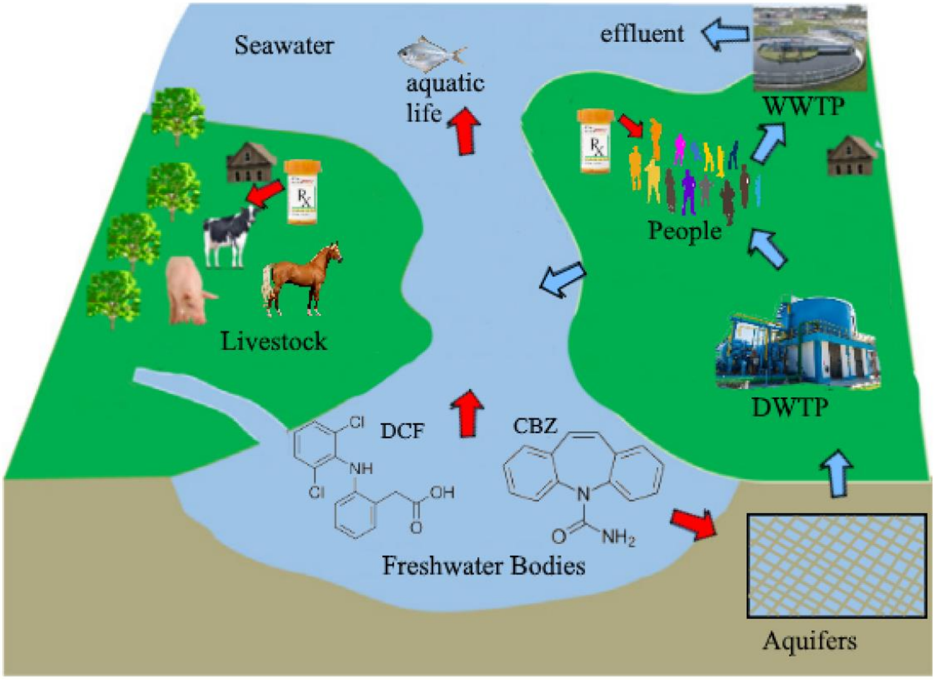


Figure 1: Graphical abstract of PPCP pathways (Tran et al. 2019)

PPCPs consist of a wide range of complex organic molecules with long carbon chains and high chemical recalcitrance. Such emerging contaminants are often poorly, or not at all, treated by conventional WWTPs (Drewes et al. 2003) leading to an emerging field of study in best methods to treat wastewater effluent which still contains ECs. Soil aquifer treatment (SAT) is a promising method of treating WWTP effluent which still contains pharmaceuticals (Barbagli et al. 2019). Two pharmaceuticals are the focus of this study: diclofenac (DCF) ($C_{14}H_{11}Cl_2NO_2$), a non-steroidal anti-inflammatory drug which is common in municipal, agricultural, and natural waterways, and carbamazepine (CBZ) ($C_{15}H_{12}N_2O$) which is an antiepileptic drug found in municipal and natural waterways (Figure 2).

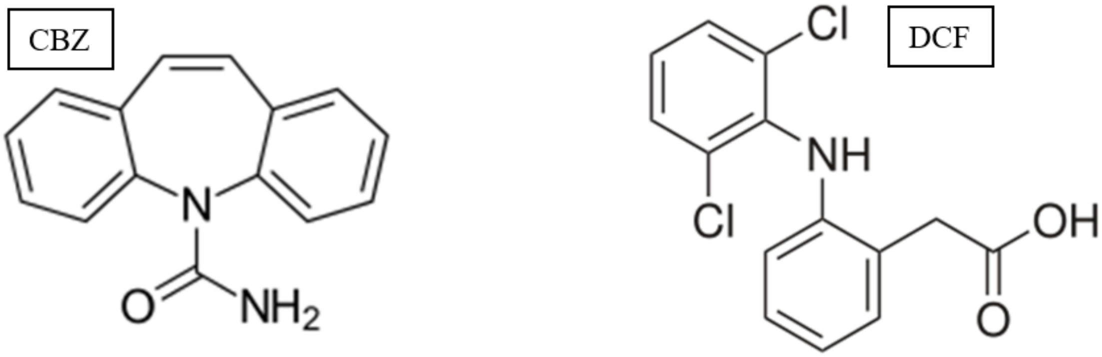


Figure 2: Chemical Structures of CBZ and DCF

Due to the prevalence of these two drugs in water supplies across the United States and the rest of the world, some researchers have proposed that either of these drugs could be used as a marker for the presence of other pharmaceuticals in a body of water (Tran et al.

2019)(Zhang, Geißen, and Gal 2008)**.** An additional benefit of using both of these drugs specifically as markers is that CBZ is a polar molecule and DCF is a non-polar molecule. By analyzing for both, the effects of chemical polarity on the fate and transport of other PPCPs, and biases of polar or non-polar substances in a passive treatment system such as SAT may be better distinguished.

SAT is often used as a polishing step for tertiary wastewater effluent, where the water is discharged into a spreading basin under controlled conditions allowing the effluent to percolate naturally through the soil (Mansell and Drewes 2004). During SAT, effluent contaminants such as pharmaceuticals are removed and eliminated through a combination of adsorption to soil and biodegradation by the soil microbiome (Martínez-Hernández et al. 2016), such biologic degradation may vary from processes observed in activated sludge treatment in WWTPS. Adsorption is a surface process wherein compounds, referred to as sorbates, adhere to the surface of another substance called the adsorbent. It is a component of the general term sorption, which refers to the combination of absorption, the chemical integration of a compound into a bulk substance, and adsorption. PPCPs adhere, or adsorb, to the surface of soil particles. PPCPs adhere, or adsorb, to the surface of soil particles. PPCPs demonstrate different adsorption affinities for soil particles depending on the soil classification, particle size distribution, and chemical properties (i.e., presence of organic matter). Beyond the physiochemical interactions, there are biological interactions which enable SAT to function. Soils with higher soil organic carbon (SOC) fractions are generally observed to have a denser and more active soil microbiome (Lucas and Weil 2021). The presence of an active soil microbiome can promote both the adsorption of organic constituents like PPCPs and also facilitate biochemical degradation via reductive dechlorination (Coutinho et al. 2018).

Another process important to the performance of SAT systems is the effect of soil saturation and or drying and wetting cycles. In natural systems, drying and wetting cycles are governed by precipitation and evaporation, but in SAT systems these cycles are carefully controlled to increase efficiency. Maximum temperature during drying and the rate of change in temperature are all shown to affect the mobility and persistence of complex organic compounds in soil media (Seol and Lee 2001). Studies of these effects are critical to optimal SAT performance but require equipment and time beyond the capabilities of this study.

Because SAT systems are complex and ECs present unique challenges, SAT feasibility studies require extensive research and laboratory experimentation. Effective SAT requires a comprehensive understanding of the physiochemical properties of the soil, potential biotransformation of these compounds, along with the interactions of different pharmaceuticals within the given hydrogeologic setting. Some experiments may be conducted at a small scale (laboratory) to characterize one specific property, while other experiments may involve pilot or field scale studies for more holistic analyses of contaminant fate and transport. Even at a pilot-scale such characterization is very time demanding, and can take months or years to determine the viability of an area for use in SAT (Wu et al. 2021) (Shabani et al. 2020) (Drewes et al. 2003). This study aims to investigate how the SAT site characterization process may be streamlined by determining the scalability of lab studies for adsorption of pharmaceuticals in water to soil. This determination was made by identifying the consistency of findings across common lab experiments relating to SAT characteristics independent of experimental scale. If the lab scale results from experiments conducted for this thesis are consistent with behavior observed at the larger scale, then going forward it may be possible to reduce the required time for SAT site characterization by running more lab scale experiments and fewer time-consuming pilot or field scale experiments and characterizations.

Agreement between breakthrough curves and adsorption isotherms (Poursaeidesfahani et al. 2019) would suggest the validity of smaller scale lab experiments to determine SAT efficiency for these conditions. A lack of agreement between the isotherms and breakthrough curves would present similarly interesting results, potentially indicating the effects of micro and macropores in soil structure, effects of scale on soil organic content, or other unknowns which would merit further study in a future project. In large scale columns the contact time between influent and soil is expected to be much greater than in the bench columns, because these experiments were not able to maintain a constant empty bed contact time (EBCT). Increased experimental scale will also increase spatial heterogeneity which could cause inconsistent removal of contaminants. This increased heterogeneity may increase advective dispersion of the contaminants and reduce effects of molecular diffusion.

2. LITERATURE REVIEW

This chapter expands on the concepts presented in the Introduction by reviewing other studies deemed relevant to this research. First, a deeper characterization on carbamazepine and diclofenac contamination in aquifers, surface water, and wastewater was conducted. Then, the efficacy of traditional wastewater treatment for removing pharmaceuticals was explored. Physiochemical properties of diclofenac and carbamazepine were investigated, along with the scale and methods of such studies.

2.1 Characterization of CBZ And DCF Contamination in Aquifers and Wastewater

WWTPs are consistently identified as being unable to treat, or fully eliminate, many emerging contaminants (ECs). Emerging contaminants in wastewater are loosely characterized as synthetic or natural contaminants which historically have not been monitored or detected, but are now suspected to pose risks to the environment and/or human health. Classes of emerging contaminants include but are not limited to: PPCPs, artificial sweeteners, fertilizers, nanomaterials, per-fluoroalkyl substances (PFAS), radioactive materials, and nanomaterials. Focusing on PPCPs, pharmaceuticals like DCF and CBZ are some of the most frequently detected in surface waters and wastewaters, but sulfamethoxazole, gemfibrozil, ketoprofen, triclosan, and acetaminophen are also popular targets of PPCP research due to their high consumption and poor removal (He, Echigo, and Itoh 2016). The subset of PPCPs also include various hygiene products and hormones which are classified as endocrine disrupting compounds and can interfere with development and reproduction in aquatic organisms. Chemical formulas of these compounds vary significantly, but are generally characterized by having long carbon chains and aromatic rings leading to increased chemical recalcitrance (Martínez-Hernández et al. 2016).

Production and consumption of PPCPs is steadily increasing both domestically and globally, while analytical methods and technologies become more advanced. As a result of these factors, there has been a significant increase in detection of such compounds in surface waters, municipal water supplies, and groundwater aquifers, with United States aquifers ranging from pharmaceutical detections between 5-15% (Figure 3) (Bexfield et al. 2019).

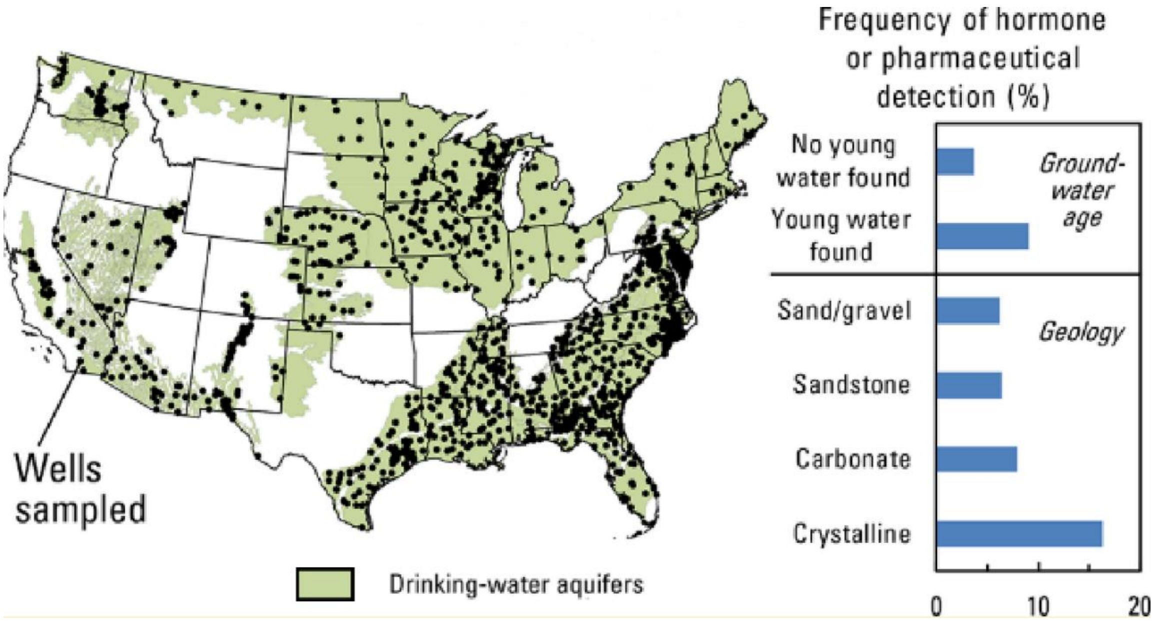


Figure 3: Detection of hormones and pharmaceuticals in United States drinking water aquifers from (Bexfield et al., 2019)

Widespread production and consumption of these compounds results in a wide range of sources for PPCPs to potentially enter the environment and water supplies. Pharmaceutical drugs are prescribed to people who eventually excrete such compounds and their metabolites into sanitary systems which are then processed at WWTPs. A study in the United Kingdom also highlighted the degree to which unused pharmaceuticals were improperly disposed of by patients, who often would flush unused pills down toilets or discard of them in household waste (Bound and Voulvoulis 2005). Prescription and usage frequency is not the most important predictor of PPCP occurrence, however; the chemical properties controlling absorption upon consumption, resistance to water treatment, and persistence in the environment have been shown as the most important variables. A review of the 200 most prescribed pharmaceuticals in the US in 2007 did not contain any of the most commonly detected drugs in treated water, nor was the most prescribed drug detected in any treated water (Benotti et al. 2009). The most commonly prescribed drugs appear to be more fully metabolized by humans and animals, or readily degradable in the environment or by conventional water treatments.

Water containing PPCPs is treated and discharged into surface waters or aquifers without significant elimination of treatment-resistant PPCPs. Carbamazepine, in particular, is one of the most commonly detected PPCPs in groundwater, due in part to its recalcitrance in typical WWTP processes such as activated sludge (Drewes et al. 2003). Pharmaceutical drugs are also increasingly present in agriculture where they are given to livestock at massive scales to reduce infections or mitigate physical ailments. Livestock then excrete the compounds or metabolites, which can remain on the surface until carried off by precipitation runoff, or seep into the ground and infiltrate aquifers. Estimates of total PPCP load excreted by livestock are in the thousands of tons per year (Kemper 2008).

A significant portion of research studying PPCP presence in surface or groundwater discusses either CBZ or DCF as a result of their high usage and low removal efficiency (Zhang et al. 2008) (Silver et al. 2018). For aquifers or bodies of water which are also used for water supply and contain such compounds, water contaminated with CBZ or

DCF may be extracted and subjected to water treatments that have been proven as ineffective at degradation or removal of the compounds in both drinking water treatment plants (DWTPs) and WWTPs (Simazaki et al. 2015) (Phonsiri et al. 2019).

Incompletely treated wastewater still containing PPCPs is then discharged through various environmental pathways, ending up in surface waters and groundwater. In surface waters PPCPs, especially endocrine disrupting compounds, can impose adverse effects on aquatic life (Lei et al. 2020). Water directly injected into aquifers for municipal use can also retain PPCPs (Bexfield et al. 2019), which may then be consumed by humans; however, presently identified PPCPs in municipal drinking water are well below concentrations deemed pharmacologically relevant (Simazaki et al. 2015), or that they are well below concentrations deemed toxic to human health and development. Discharge of WWTPs into surface waters or groundwater, and incomplete elimination in DWTPs indicates that the total presence of PPCPs in water supplies will continue to increase over time unless methods are applied which directly address the removal of these ECs from treated water. These processes are sometimes referred to as tertiary, advanced, or polishing treatments, which occur after conventional water treatment processes.

In the absence of advanced treatments, PPCPs begin to accumulate in natural water reservoirs like groundwater aquifers, and, at present, do not have federally regulated permissible concentration levels. However, nine endocrine disrupting compounds are on an EPA “watch list”, which the EPA defines as “ water contaminants that are known or anticipated to occur in public water systems and are not currently subject to EPA drinking water regulations” (U.S. EPA 2018). A USGS study (Bexfield et al. 2019) began a national scale assessment of PPCPs in aquifers used for municipal water supply. Samples were collected from over 1000 sites in aquifers which supply municipal drinking water, and in 5.9% of samples at least one of the surveyed compounds was identified. CBZ was present in at least 0.5% of these samples. DCF was not a targeted compound, and its detection frequency was not reported. This study targeted a wide range of PPCPs, and reveals a detection rate of CBZ that is much lower than other studies focusing on CBZ specifically (Chefetz, Mualem, and Ben-Ari 2008; Jurado et al. 2014; Zhang et al. 2008). This may be an indication that the geologic conditions of aquifers across the United States have a significant impact on the attenuation of CBZ, or that WWTP infrastructure varies substantially across regions of the country and only a few WWTPs are unable to treat CBZ. Wastewater treatment plant effluent has been shown to be a primary contributor of pharmaceuticals to ecosystems and bodies of water, highlighting the difficulties of treating PPCPs through conventional methods such as activated sludge treatments or trickling filters (Benotti et al. 2009). Due to the broad scale of the study geographically and the number of surveyed compounds, detection limits for any single compound are likely to be much higher than in studies focusing on only a handful of PPCPs.

2.2 PPCP Properties and Treatment Challenges

A majority of wastewater and drinking water treatment plants are designed for the efficient removal of common legacy pollutants like dissolved solids, nutrients, biodegradable organics, nitrates, and pathogens (bacteria and viruses). Conventional drinking and wastewater treatment processes like chlorination and sedimentation-flocculation, aeration, and filtration can remove these legacy contaminants but are largely ineffective at addressing more complex synthetic organic compounds like PPCPs and other ECs. Reviewing the extensive literature studying removal efficiencies of different PPCPs around the world reveals that removal is largely determined by the presence or absence of advanced treatment of WWTP effluent (Khasawneh and Palaniandy 2021). For aquifers or bodies of water which are also used for municipal water supply, source water can be contaminated by PPCPs like CBZ or DCF from incompletely treated WWTP effluent, which will then go through drinking water treatments which have been shown as ineffective at degradation or removal of such compounds. An assessment of PPCPs in drinking water supplies revealed CBZ was present in more than 1/3 (n=15) of the surveyed systems for municipal water distribution in the United States (Benotti et al. 2009). Additionally, CBZ and DCF were two of the seven PPCPs out of 64 studied, which were not removed by conventional DTWP processes (Simazaki et al. 2015). Ozonation and engineered membranes are examples of advanced treatments which can occur at WWTPs, while SAT is an example of an external advanced treatment (Shabani et al. 2020).

CBZ and DCF are consistently identified as highly recalcitrant PPCPs in conventional WWTP treatments (Tran et al. 2019) (Simazaki et al. 2015), because they are also widely consumed these two PPCPs are included in many peer-reviewed studies on PPCP presence in effluents. Surveyed WWTPs in (Zhang et al. 2008) generally show a detection ratio of 100% for both CBZ and DCF, indicating that both drugs were detected in all samples of treated effluent. WWTP removal efficiencies ranged from 0% to 80%, but most typically below 40% for DCF and below 10% for CBZ. Approximately 40% of surveyed plants indicated no removal of CBZ, and 17% reported no removal of DCF (Figure 4).

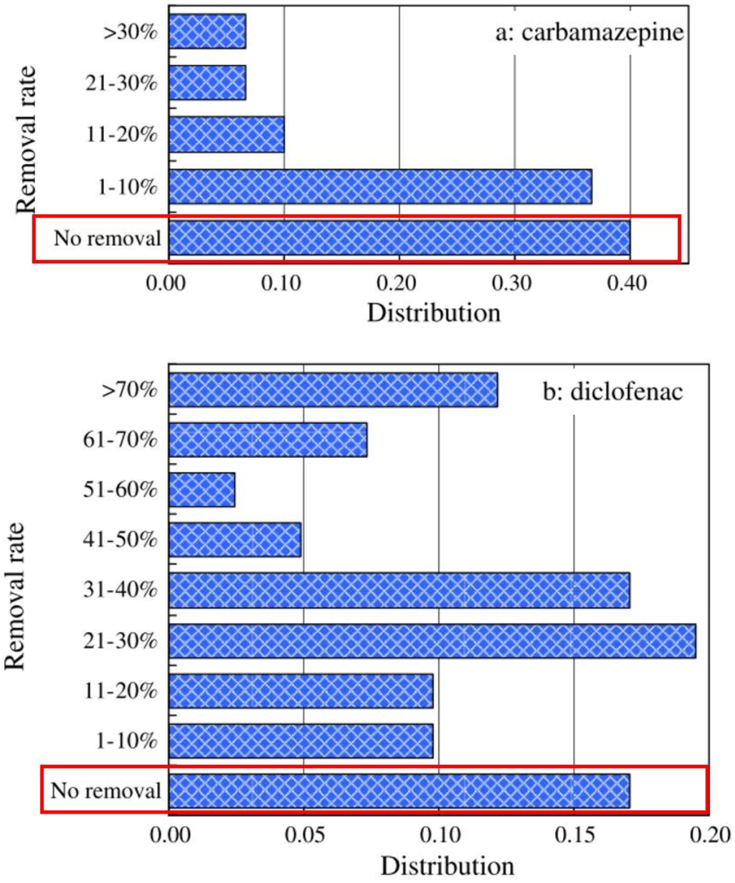
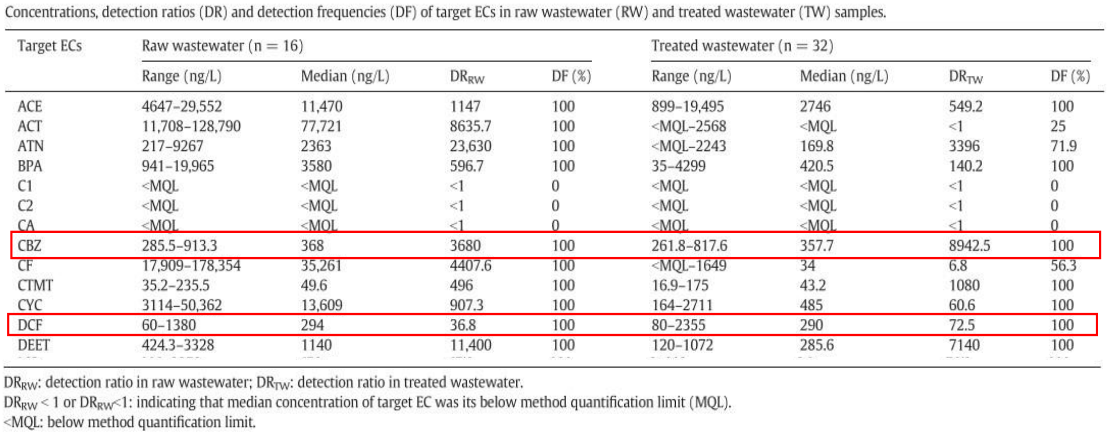


Figure 4: Findings on WWTP removal of CBZ and DCF derived from analysis of 19 separate peer-reviewed studies (Zhang et al. 2008).

No mention of advanced treatments were made in this study, which emphasized that conventional activated sludge treatments were very ineffective at removing CBZ, and only slightly more effective at removing DCF. It concluded that short-term or rapid biodegradation can eliminate DCF, but not CBZ. The highest removal of CBZ was in a plant which added a silicone oil to the activated sludge.

A similar 2019 study in Singapore characterizing emerging contaminants in wastewater before and after treatment illustrates the inefficiencies of WWTPs for EC removal, shown in Table 1.

Table 1: Detection frequency of emerging contaminants in wastewater from (Tran et al. 2019).



Concentrations, detection ratios (DR) and detection frequencies (DF) of target ECs in raw wastewater (RW) and treated wastewater (TW) samples.

Target ECs	Raw wastewater (n = 16)				Treated wastewater (n = 32)			
	Range (ng/L)	Median (ng/L)	DR_{RW}	DF (%)	Range (ng/L)	Median (ng/L)	DR_{TW}	DF (%)
ACE	4647–29,552	11,470	1147	100	899–19,495	2746	549.2	100
ACT	11,708–128,790	77,721	8635.7	100	<MQL–2568	<MQL	<1	25
ATN	217–9267	2363	23,630	100	<MQL–2243	169.8	3396	71.9
BPA	941–19,965	3580	596.7	100	35–4299	420.5	140.2	100
C1	<MQL	<MQL	<1	0	<MQL	<MQL	<1	0
C2	<MQL	<MQL	<1	0	<MQL	<MQL	<1	0
CA	<MQL	<MQL	<1	0	<MQL	<MQL	<1	0
CBZ	285.5–913.3	368	3680	100	261.8–817.6	357.7	8942.5	100
CF	17,909–178,354	35,261	4407.6	100	<MQL–1649	34	6.8	56.3
CTMT	35.2–235.5	49.6	496	100	16.9–175	43.2	1080	100
CYC	3114–50,362	13,609	907.3	100	164–2711	485	60.6	100
DCF	60–1380	294	36.8	100	80–2355	290	72.5	100
DEET	424.3–3328	1140	11,400	100	120–1072	285.6	7140	100

DR_{RW}: detection ratio in raw wastewater; DR_{TW}: detection ratio in treated wastewater.
$DR_{RW} < 1$ or $DR_{RW} < 1$: indicating that median concentration of target EC was its below method quantification limit (MQL).
<MQL: below method quantification limit.

Detection ratio (DR_{RW}, DR_{TW}) and Detection Frequency (DF %) for 31 ECs in raw and treated wastewater are reported. Detection ratio is calculated as the ratio between average EC concentration and method detection limit.

Referring to Table 1 indicates the median concentrations of CBZ (368 ng/L raw, 357.7 ng/L treated) and DCF (294 ng/L raw, 290 ng/L treated) are barely reduced throughout conventional WWTP processes. Persistence to traditional WWTP processes as shown here illustrate why treated WWTP effluent is one of the leading causes of PPCPs in surface and groundwater (Jurado et al. 2014).

Across SAT literature detailing removal of pharmaceuticals like CBZ and DCF, phrasing can be unclear on the definition of removal as a whole. In some cases removal can refer to the amount of the compound which is adsorbed to soil media (Williams, Watson, and

Nelson 2014), while others only consider removal to be the chemical breakdown and degradation of a compound that has adsorbed to media (Silver et al. 2018). For studies where soil is reexamined after experimentation (Silver et al. 2018) (Martínez-Hernández et al. 2016) (Onesios and Bouwer 2012), the distinction between adsorption and degradation can be made. Studies exploring the removal of pharmaceuticals in SAT systems (Onesios and Bouwer 2012) most commonly refer to removal as the degradation or breakdown of compounds in media that has been used for treatment. The chemical degradation of these compounds is understood to primarily result from microbial activity in soil media, which is indirectly a result of wetting and drying cycles of soil media determining whether biological processes are either aerobic or anaerobic (Silver et al. 2018). Microbial activity is well understood to be affected by drying and wetting of soils, where some microbes that can only survive in saturated environments cannot survive in dry soils. Some microbes can only survive in dry soils, and some are most efficient in intermediate vadose zones. These traits have also been shown to cause a strong response in soil microbes where the saturation of a soil may kill off aerobic microorganisms, which can then serve as a labile carbon source for anaerobic microbes and increase their degradation of compounds in the soil (West, Sparling, and Speir 1989).

Across reviewed literature, soils with a higher organic content were shown to remove more pharmaceuticals from the mobile phase (Chen, Liu, and Chen 2017) (Zhao et al. 2012) (Laws et al. 2011). This trend can be explained by the increase in microbial biomass in soil media, along with physiochemical properties of contaminants such as the octanol water partition coefficient (K_{OW}) and octanol water distribution coefficient (Ilyas, Masih, and van Hullebusch 2021). The K_{OW} parameter is the ratio of target concentration at equilibrium in octanol, a non-polar lipid, versus its concentration in water which is polar; this parameter is also commonly presented as the base 10 logarithm of this ratio (Log K_{OW}) and is considered a strong indicator of a given compound's affinity for organic matter (Mansell and Drewes 2004). A related parameter is the organic carbon distribution coefficient K_{OC} or $\log_{10} K_{OC}$. While K_{OW} should be an intrinsic property of chemicals, inconsistencies are present in the reported values for CBZ and DCF. Experiments aiming to address these variabilities were conducted by a university in Berlin in conjunction with the German Federal Institute for Risk Assessment, which ultimately presented values of log K_{OW}= 1.90 for DCF, and log K_{OW}= 1.51 for CBZ (Scheytt et al. 2005), but more recent studies have still reported different values. Values for K_{OC} present just as much or more variation in reported values across literature (Table 2). This may be a result of the different organic substances present in soils (e.g., cellulose, lignin, and humic substances) increasing the variability of results when compared to a single organic compound such as octanol.

Table 2: Range of reported values for log KOC and log KOW for CBZ and DCF from surveyed literature

Reference	CBZ		DCF	
	log K_{oc}	log K_{ow}	log K_{oc}	log K_{ow}
(Scheytt et al. 2005)		1.51		1.9
(He et al. 2016)	2.71		2.39	
(Jurado et al. 2014)		2.77-3.64		
(Chefetz et al. 2008)	2.45-2.32		1.79 - 2.22	
(Silver et al. 2018)		2.25 - 2.45		4.02 - 4.50
(Barbagli et al. 2019)	1.8-2.9	2.25 - 2.45	1.9 - 2.3	4.51 - 4.57
Maximum Range	**1.8 - 2.71**	**1.51 - 3.64**	**1.9 - 2.39**	**1.9 - 4.57**

Such a wide range in reported values makes it difficult to use the log K_{OC} and log K_{OW} values alone as predictors of PPCP behavior in the environment. This variability also suggests that a determination of these values via experimentation may not be the most effective method for comparing results across studies or experiments.

2.3 Benefits and Applications of SAT

Analysis of the difficulties in managing and treatment of PPCPs prompts the question of what is the best way to deal with these emerging contaminants? SAT is one method of addressing these contaminants which is growing in popularity, with the EPA citing it as the most cost-effective method for potable reuse of water (U.S. EPA 2018). One of the largest costs of operating water treatment facilities is the energy required to drive advanced-treatment filtration mechanisms (Sabet et al. 2019). Environmental nanotechnology is one active area of research for the potential to reduce energy expenditures in water treatment processes through nano-filtration and nano-membranes (Pavlović et al. 2010), or to enhance treatment efficacy at earlier stages of treatment with engineered nanoparticles (Cruz-Silva et al. 2019). However, the costs to develop and manufacture nanomaterials can pose a high barrier to widespread adoption. SAT circumvents many of these difficulties and expenses, as the removal of contaminants occurs naturally through gravity driven flow in porous media. Energy is still necessary to transport WWTP effluent from the source to a SAT site, but this requires much less sophisticated infrastructure and less energy, especially when existing topography can alleviate energy requirements for water transport downgradient. After SAT, water may then be recovered from the aquifer for use, and treated again before distribution

(Grinshpan et al. 2021). Figure 5 depicts a typical SAT treatment train where municipal wastewater is collected and treated by a WWTP, which then discharges partially treated wastewater into a basin, from which water can later be recovered and treated.

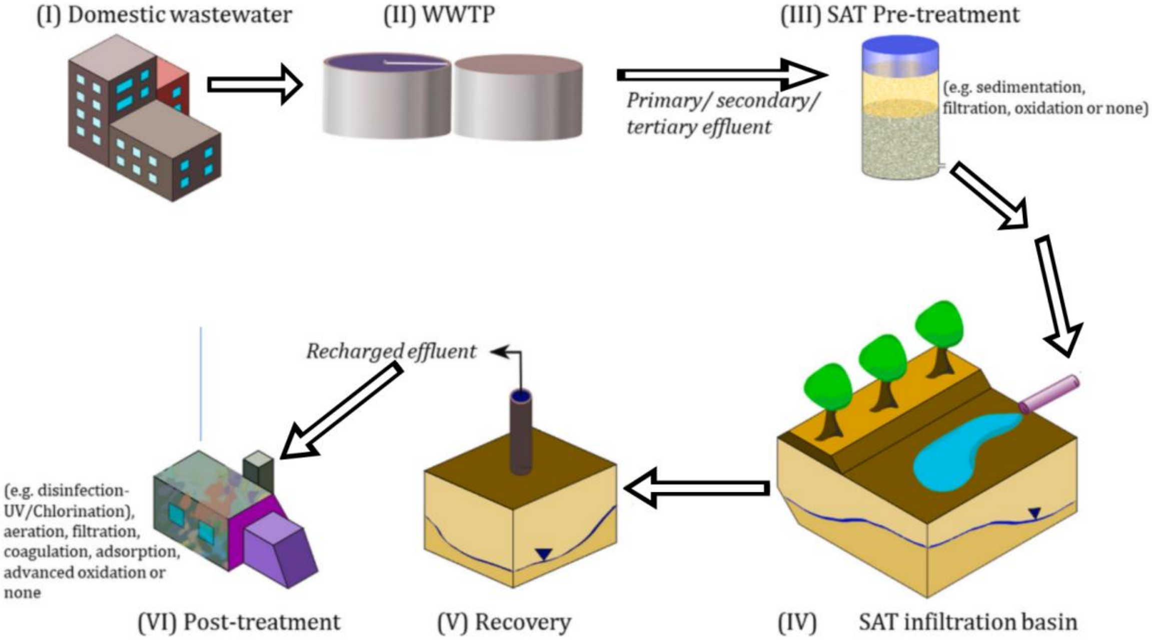


Figure 5: Typical SAT Schematic from (Grinshpan et al., 2021)

Water scarcity is becoming increasingly apparent as populations continue to grow and land use continues to shift (Wallander, Aillery, and Schaible 2015). As populations increase so too does their consumption of potable water and generation of wastewater. Aquifer recharge is a popular method of addressing water scarcity, and soil aquifer treatment has shown promise as a cost and energy effective recharge method with high potential for removal or degradation of PPCPs under the right conditions. As clean water becomes scarcer and wastewater becomes more plentiful, SAT shows promise as an effective and cost-efficient method to simultaneously address these issues. Several pilot studies have been funded to assess SAT feasibility and performance in PPCP removal

(Coutinho et al. 2018) (Mansell and Drewes 2004). The city of Los Angles is one notable investor, where the city Bureau of Sanitation and Department of Water and Power funded to a two-year pilot study into large scale SAT feasibility (Shabani et al. 2020).

As promising as SAT appears this method has its drawbacks: natural systems may be less effective than highly specialized and engineered approaches such as environmental nanotechnology. Many studies have proven the efficacy of engineered nanoparticles in addressing PPCP contamination (Aydın et al. 2021), but the increased adsorption per unit mass in engineered nanomaterials comes at the cost of higher operational costs and challenges in scalability. Non-engineered media such as the soils used in SAT are less effective per unit mass, but the sheer volume and availability of soil, however, may compensate for reduced efficiency. One study examined the fate of endocrine disrupting compounds in a SAT system over thirteen years and observed no breakthrough of any studied compounds (Mansell and Drewes 2004).

Effective SAT requires a fundamental understanding of general soil physiochemical properties so that suitable soils for SAT can be determined along with their expected performance. Generally, finer grained soils permit more adsorption than coarse grained soils (Martínez-Hernández et al. 2016). A fine-grained soil has substantially greater surface area per unit volume than a coarse-grained soil, and because adsorption occurs at the surface of a substance, this means there is more surface area for adsorption to occur. Chemical compositions of soils are also critical; sand is generally composed of silica or SiO_2 which is inert at atmospheric conditions. Clayey soils contain more clay minerals, composed of various aluminosilicates which are more reactive than SiO_2. Aluminum in these soils can form complexes with organic constituents such as those in PPCPs, removing them from the liquid phase through surface complexation and adsorption (Zhao et al. 2012). Clay particles also carry a net-negative surface charge, which can correspond to affinity for charged and polar substances. Organic soils have similar chemical effects, where soil organic carbon (SOC) is reactive in atmospheric conditions and also allows for surface complexation and increased adsorption in soils (Chefetz et al. 2008). Because of these properties, soils with higher contents of clay or organic matter are widely understood to allow for much greater adsorption per unit volume than coarser or more silicate rich soils, but reduced permeability of these soils makes SAT more difficult. SAT is a category within Indirect Potable Reuse (IPR), which the US EPA defines as the use of "highly treated municipal wastewater as a municipal drinking water source" incorporating some form of environmental buffer (U.S. EPA 2018). As the name suggests, in SAT soil from the surface down into aquifer material is the requisite environmental buffer. Under ideal soil conditions, ECs are physically adsorbed to soil surfaces and chemically degraded by bulk soil chemical properties or microbial communities as they pass downwards through the soil and into an aquifer where water will eventually be pumped for IPR.

Drying/wetting cycles are another important parameter to SAT performance as depicted in Figure 6 (Silver et al. 2018). Wetting soils leads to saturation and anoxic conditions, which can affect the active microbial communities in a soil. Under anoxic conditions denitrification can occur, which is observed to heavily degrade some PPCPs while not affecting others (Drewes et al. 2003). Similarly, unsaturated or aerobic conditions are also shown to be more effective for some PPCPs than others (He et al. 2016).

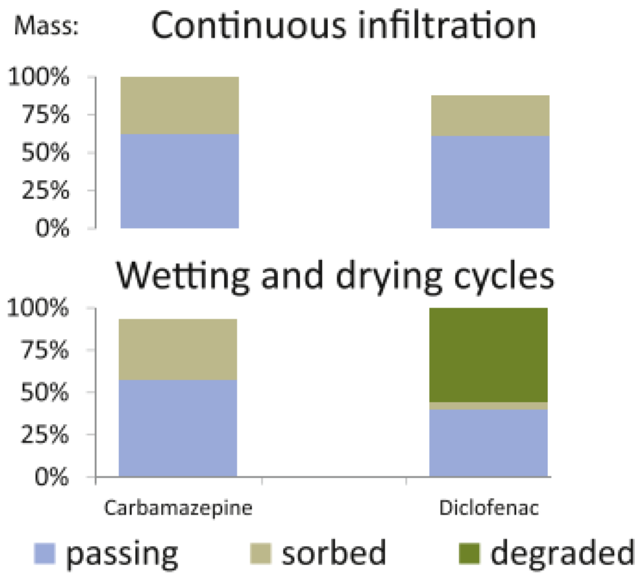


Figure 6: Effects of Drying and Wetting Cycles on pharmaceutical attenuation from (Silver et al., 2018)

2.4 Importance of Experimental Scale in Studies

There is an abundance of research being conducted on the occurrence and potential removal of PPCPs and other ECs being conducted globally. Fundamentally though, any researcher understands that results of controlled lab experimentation rarely present the same results as real-world full-scale applications. Concerning the treatment of PPCPs in wastewater, some researchers (Chen et al. 2017) believe the most important experiments are those at the highly controlled small-scales, where it is possible to control for many variables and isolate key responses in PPCP-soil interactions. There is undoubtedly credence to this belief – with the existing volume of research on ECs in the environemnt, there is consensus on some of the driving factors to EC treatment: source water quality, soil mineralogy, organic carbon presence, and EC hydrophobicity for example. By identifying these properties and utilizing geospatial datasets and contaminant properties, substantial potential exists for the development of utilities to determine preliminary feasibility of SAT systems globally. A limited-scale proof of concept study attempted this in the vicinity of Athens, Greece (Figure 7) (Tsangaratos et al. 2017).

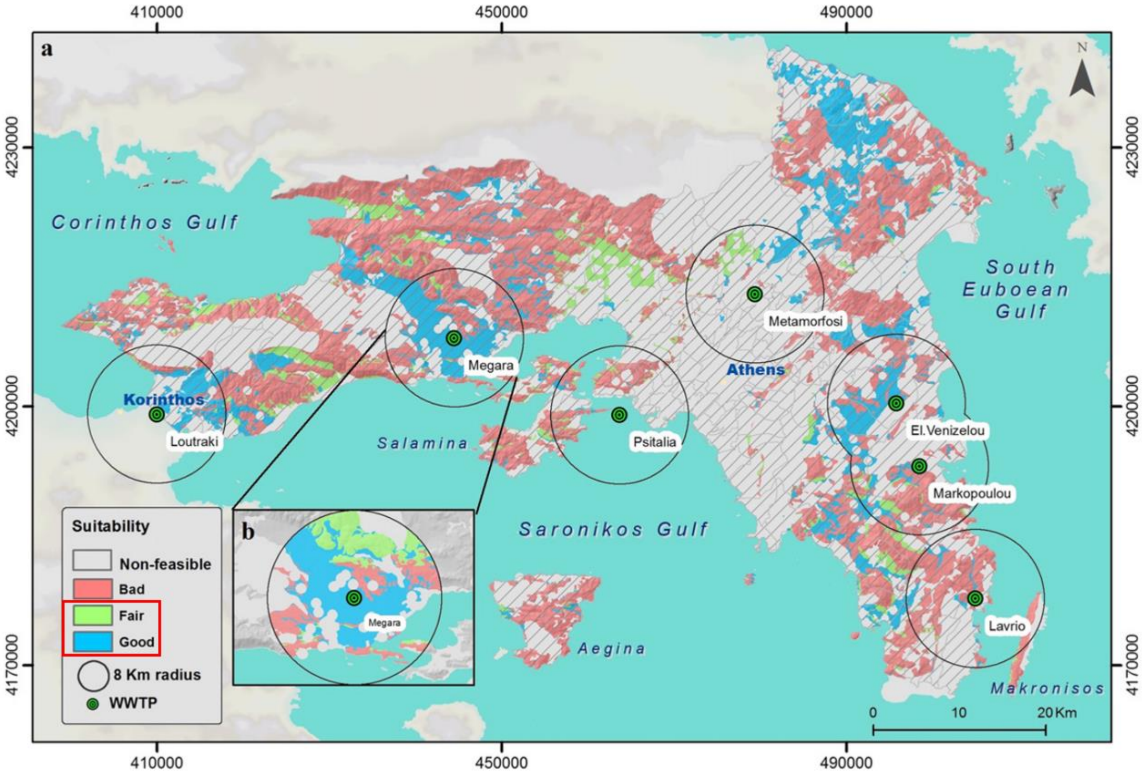


Figure 7: Potential for SAT feasibility assessment at large scales using geospatial and contaminant data (Tsangaratos et al. 2017)

Figure 7 emphasizes feasibility from a regulatory standpoint such as zoning, ease of access, and proximity to treatment plants, but also explores the environmental feasibility. Properties such as regional geochemistry, typical permeability, surface slope, and depth to groundwater are also factored into a weighted decision matrix. As a more robust and parameterized dataset for physiochemical requirements of SAT is developed more variables could be considered in a similar weighted decision matrix: typical SOC, commonly detected EC concentrations, EC properties, etc.

An outline to devising a conceptual model of SAT feasibility is shown in Figure 8 (Hussaini 2021) which shows how experiments in this thesis could contribute to an enhanced set of parameters of SAT feasibility decisions.

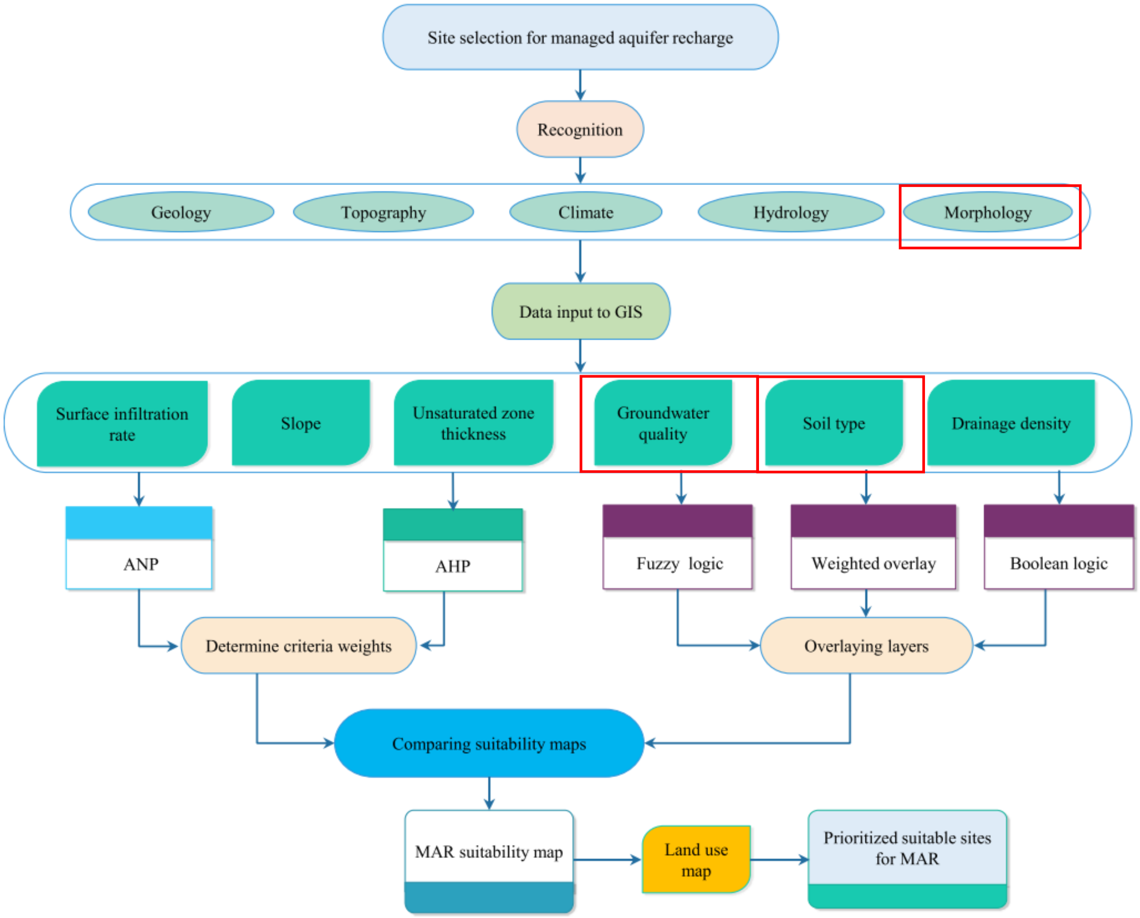


Figure 8: Schematic for devising conceptual SAT feasibility models (Hussaini, 2021)

Soil and water properties explored in this study are boxed in red

Through the combination of soil and contaminant characterizations and geospatial datasets, adaptive computer models of SAT site feasibility across large scales can be developed. Typical SAT studies such as adsorption isotherms and soil columns could contribute to development of more robust hydrologic and geochemical datasets, which can be further supported by other limiting parameters such as protected land or proximity to major pollution sources (Tsangaratos et al. 2017).

Studies focusing on further understanding some of these specific, already identified components, are critical to understanding EC behavior in SAT. Narrow-focused studies are limited however, by their inability to identify auxiliary responses to one mechanism in a more complex and variable real-world system. Conversely, pilot or field scale experiments are invaluable in the assessment of real-world SAT performance (Laws et al. 2011), but are limited in their ability to pinpoint the effects of different mechanisms at play in SAT. Some studies go so far as to explicitly state that their chosen scale of experiment is a better representation than others, such as Barbagli et al. (2019) which claims that column experiments produce results closer to real world data than batch adsorption isotherm studies.

There appears to be a lack of research around SAT and PPCP treatment with the explicit goal of comparing different experimental scales under one study. There also appears to be desire for studies like this shown by meta-analyses like Ilyas et al. (2021), which attempts to predict PPCP behavior in the environment using K_{OW} and K_{OC} values. Potential applications to a system or methodology combining results of diverse types of studies would prove extremely valuable in SAT research.

3. METHODS

This section details the procedure for each of the three experiments conducted: adsorption isotherm jar arrays, bench columns, and large-columns, and how data was processed. For this study, removal is considered any decrease in compound concentrations in the mobile phase, compared to the original concentration.

3.1 Soils Characterization

Three different soils were used across all experiments: a low organic sand, a medium organic sand-topsoil blend, and a high organic sand-topsoil blend. For the low organics soil, a garey concrete sand mix was purchased from CalPortland Construction. An organic topsoil mix was purchased from a local hardware store for use in the medium and high organics soils. All soils were processed in a geotechnical laboratory in accordance with ASTM D6913 and ASTM D2487 to characterize grain size distributions, and to compare to the manufacturer provided specifications. Soil organic content (SOC) was controlled by mixing known masses of the sand with the topsoil, and hand-mixing to ensure homogeneity in the soil mixtures. By characterizing the organic content in both undiluted topsoil and the two soil blends, the high organic topsoil could be effectively diluted (Oldfield, Wood, and Bradford 2020) to 20% and 40% for the medium and high organic soils, respectively. Organic topsoil was purchased in 1 ft^3 bags. Sand and topsoil were measured by weight in large buckets in 20-pound increments then added to large plastic tubs which each stored 80 pounds of a soil blend. During this mixing process, care was taken to manually break up any large aggregate clumps of topsoil and to remove any unwanted foreign debris. To determine the percent organics in the topsoil and topsoil blends, Method A of ASTM standard method D2974-20 was used. Approximately 50g of soil was collected from both topsoil blends and from the pure topsoil. Samples were dried and weighed, then placed in a muffle furnace at 440°C for 1 hour and weighed again post ashing. By conducting these measurements for both soil blends and the undiluted topsoil, results of SOC analysis also confirmed the validity of the soil mixing method. Characterization of the three soils is presented in Table 3, along with properties of the topsoil used to produce soil blends. Full sieve analyses for each soil and the pure topsoil are presented in A. Soil Characterizations.

Table 3: Soil Characteristics

Soil Name	Composition	Gravimetric Water Content	Organic Content	Porosity Estimate*
Sand	100% Concrete Sand	4.1%	0%	34%
Medium Organics	80% Concrete Sand 20% Organic Topsoil	13.0%	8%	48%
High Organics	60% Concrete Sand 40% Organic Topsoil	24.2%	17%	56%
Topsoil for Blending	100% Organic Topsoil	90.0%	54%	--

Porosity values represent estimates described in Section 3.5, not an ASTM standard method. Topsoil was not measured in this experiment, so no estimate is given.

3.2 Reagents

Diclofenac salt and Carbamazepine salt were purchased from Fisher Scientific and dissolved in pure methanol to prepare stock solutions, which were then diluted with DI water as needed for experiments. The following HPLC grade reagents were also purchased from Fisher Scientific: acetic acid, acetonitrile, and methanol.

3.3 Isotherms

Adsorption isotherm experiments were conducted by adding 50g of soil to a set of screw-top square jars. To ensure that biological processes were not occurring over the duration of the experiment, each of the 15 isotherm jars was filled with soil, then placed in an autoclave for 15 minutes to ensure sterilization of both the jars and the soils. Into each jar, 50mL of CBZ or DCF solution was added in initial concentrations of 10 mg/L, 25 mg/L, 50 mg/L, 75 mg/L and 100mg/L. For each experiment, 160mL of each solution was produced so that 50mL could be added to each of the three jars with a few milliliters of the solution reserved for calibration curves. Data was collected in triplicate, with three jars containing the same initial concentration to enhance data confidence, for a total of 15 jars per experiment. Isotherms were prepared for each of the three soils (sand, 20% topsoil and 40% topsoil), for both DCF and CBZ.

After preparing and inoculating each of the jars they were taped together standing upright in a 3x5 array, then placed in a shaker table (*Thermo Fisher Sci 3530: Lab-Line Low Temperature Incubated Shaker*) kept at a constant temperature for six days at a constant agitation rate of 150rpm. Temperatures were not kept explicitly constant between experiments, but are all were in the range of 22-25 °C which is not expected to cause significant difference in results. Samples were left on the shaker and sampled in approximately 48-hour intervals, three times per experiment, to ensure that the time for equilibration was reached for each treatment. To collect samples from the jars, individual pipettes and filters were used to transfer supernatant from each jar to a labelled HPLC vial, which were sealed immediately and analyzed in the HPLC within 24 hours of collection. These data were then plotted as linear, Langmuir and Freundlich isotherms to determine the best fit for each treatment. These equations are as follows, where q_e represents x/m or the mass in mg of adsorbed contaminant at equilibrium per g adsorbent, and C_e represents the concentration of the contaminant in the liquid phase at equilibrium.

$$q_e = \frac{x}{m} = K_d C_e \qquad (Equation\ 1)$$

$$q_e = \frac{x}{m} = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (Equation\ 2a)$$

$$q_e = \frac{1}{q_0} + \frac{1}{K_L q_0 C_e} \qquad (Equation\ 2b)$$

$$q_e = \frac{x}{m} = K_F C_e^{\frac{1}{n}} \qquad (Equation\ 3a)$$

$$log(q_e) = log(K_F) + \frac{1}{n} log\, C_e \qquad (Equation\ 3b)$$

The standard linear isotherm equation (Equation 1) has no additional parameters and required no additional processing; K_d is the linear partition coefficient. To determine parameters of the Langmuir equation (Equation 2a) a linearized form of the equation (Equation 2b) was used to determine slope and intercept values using linear interpolation of data points. The Langmuir equation has a theoretical limit, the maximum number of adsorption sites in a given mass of adsorbent, represented by q_m. It also contains the term K_L which is sometimes referred to as the adsorption energy. The Freundlich equation (Equation 3a) was linearized the same way (Equation 3b). It contains the K_F term, known as the adsorption capacity, and also has an additional term “n” which is constant used as a correction factor, sometimes referred to as the adsorption intensity. (Equation 3a) Plots were prepared for each experiment with measured data points, and model fits from each of the three models. The best-fitting isotherm model was chosen as the model with the lowest RMSE value.

3.4 Bench-Scale Columns

To conduct the bench column experiments, an array of three identical glass chromatography columns, with an inner diameter of 76mm and length of 500mm, were filled with 1kg of soil each. Each column contained a unique soil type (sand, medium organic, high organic). Prior to experimentation 1L of DI water was passed through the filled columns to partially saturate the soil media. Columns could not be fully de-aired, and some air bubbles may have been present. Next, the stopcock on the outlet of each column was closed and a known volume of water was added into each column which was allowed to infiltrate until clear ponding above the soil surface was present. To estimate the porosity of soil in each column, the ponded volume in each column was subtracted from the known volume added to estimate a pore volume.

Four liters of a 30mg/L CBZ or DCF solution was prepared for each experiment. Once the soils were saturated, CBZ/DCF solution was added 100mL at a time from a graduated cylinder into each column. Below each column was a 250mL glass beaker which would continuously collect discharge from each column, along with a clean, dry 10mL beaker to collect samples (Figure 9). When the 100mL mark was approached on the larger beakers, the small beaker was placed under the outlet to collect approximately 5mL of the sample solution. From this small beaker, 2x 1mL samples were pulled with disposable syringes, and the samples were filtered through non-reactive PTFE filters into labelled HPLC vials. Samples were pulled from each column after each 100mL passed through, and the 200mL beakers were emptied and cleaned after every two samples. Of the initial 4L of CBZ/DCF solution, the most was added to the high organic soil and the least was added to the sand to account for the differences in porosity and adsorption capacity, shown in Table 6 of the results section. Samples of the initial CBZ/DCF solution were reserved to be processed in the HPLC so an outflow concentration (C) could be compared to the initial concentration (C_0) and create breakthrough curves showing (C/C_0).

Figure 9: Bench Column Apparatus

1kg of sand (left) 1kg of medium organic soil (middle) and 1 kg of high organic soil (right) in identical glass chromatography columns. Columns constantly drained into the larger 200mL beakers, while small beakers were used to collect samples approximately every 100mL.

3.5 Large-Scale Columns

To conduct the large column experiment, a series of six square PVC columns were used. Inner dimensions of the columns measure 10”x10”x69”. A piece of chicken wire screen was cut to size and placed in the bottom of each column, then a layer of coarse gravel about 3” thick was added on top of the screen. Finally, another chicken wire screen fitted with landscaping fabric was pressed into place on top of the gravel, this system formed the drainage system for the columns and to reduce potential clogging in outlet ports. These columns were filled to approximately 75% of their maximum capacity when dry, then fully saturated allowing the soils to settle and compact more naturally than their initial placement. To allow for more direct comparisons between the large columns and bench columns, outflow from the columns was collected and reported in pore volumes. To estimate the pore volume of soil in each column outlets were first blocked to prevent any water to escape. Columns were gradually saturated by adding controlled volumes of water to the top of each column using a 2-gallon bucket until they were fully saturated and water just pooled above the soil surface. Columns were then drained over several hours and the outgoing volume for each was measured. Depth of ponded water and depth of the coarse gravel filter drain were measured, then multiplied by the cross-sectional area of 0.69ft^2 to calculate the excess volume which was subtracted from the initial volume of water added. Pore volume was assumed to be the difference between the initial volume added and the excess volume. Figure 10 depicts the large column setup with six PVC columns and custom top-mounted plumbing system, powered by a submersed pump.

Figure 10: Large Column Apparatus

Governing this system was a pump in a 55-gallon drum, which was filled with model effluent. The drum interior was marked with incremental volumes then filled with water to approximately 55 gallons (209L). Then a 1L spike of 6,250 mg/L contaminant was added and mixed in, to yield roughly 210L of effluent at a concentration of 30 mg/L. A hose ran from this pipe to a PVC pipe array with six outlets leading to each column. Attached to these outlets were plumb bobs, which were used to ensure the columns would not overflow. The column apparatus consisted of two sand columns, two low organic columns, and two high organic columns. Due to the design of the plumbing system, it was not possible to run columns for both CBZ and DCF at the same time, so half of the inlet valves were shut for the first trial with DCF, then the other half was shut for the trial with CBZ. For these experiments, a constant discharge of CBZ/DCF solution with a constant concentration of 30 mg/L was fed into the columns. Outflow from each column was collected in 5-gallon hazardous waste containers with 1-gallon incremental volume markings, which were regularly dumped into a secondary 55-gallon hazardous waste drum. A 4-gallon sampling frequency was chosen, where flow would be temporarily stopped once the 4-gallon mark was reached on the hazardous waste containers, then approximately 100mL of the effluent would be collected using a clean beaker placed at the sampling ports at the base of each column before resuming flow into the waste containers. Samples were collected and processed for analysis from this 100 ml beaker as described above for the bench-scale columns.

3.6 Analytical Methods

To determine the concentrations of CBZ or DCF in the synthetic influent (water + CBZ/DCF), samples were processed using a Thermo Scientific Ultimate 3000 High-Performance Liquid Chromatograph (HPLC). Samples which were collected after passing through soil media were collected with disposable 1mL syringes, fitted with disposable PTFE membrane filters to prevent sediment from entering the HPLC, and filtered into HPLC vials. When preparing calibration curves for the CBZ and DCF HPLC methods, samples were passed through the PTFE filters to ensure no pharmaceuticals sorbed to the filters. The method used for processing the CBZ was adapted from (Heidari and Yari 2020), using an eluent composed of 10:45:45 Acetontrile:Methanol:H_2O (v/v/v) flowing at a rate of 0.50mL/min, and UV absorbance was measured at a wavelength of 287nm. For DCF, the mobile phase eluent was composed of 10:90 Acetic Acid : Methanol (v/v)(Madikizela and Chimuka 2017) flowing at a rate of 0.25mL/min, and UV absorbance was measured at a wavelength 258nm. Column oven temperature was held to 30°C for both analytical methods. Calibration curves and their R^2 values are available in C. Calibration Curves.

3.7 QA/QC

To verify HPLC method accuracy, calibration curves for CBZ and DCF were conducted before beginning experimentation, also including samples passed through PTFE filters used for sample collection to make sure no contaminant was retained. Additionally, for each isotherm experiment a new calibration curve was created using samples from each stock as mentioned in Section 3.3 Isotherms. For column trials, several samples of initial feed were analyzed and averaged for consistency, and values from averaged CBZ or DCF calibration curves were used to determine experimental concentrations.

Samples processed by the HPLC produced chromatographs with generally distinct peaks, but total absorbance (area under the peak curve) had to be manually determined. Care was taken to be as consistent as possible with interpretation of peaks in the results. The Chromeleon (v7) software for the HPLC included a utility for integration under manually defined curves or peaks; this tool was used to find the measured UV absorption at a specific wavelength by taking the area under chromatograph peaks. Peaks were considered to begin where absorbance was at least 3x greater than small peaks from signal noise and ended where the signal returned to the absorbance level determined at the start of the peak (a horizontal line across the chromatograph). In some cases, peaks contained “shoulders” or smaller peaks within the peak extents, which were considered to be all part of one peak. For samples where the absorbance remained higher after the peak than the beginning peak absorbance, the end of the peak was considered to be the point where the chromatograph reached this new steady value. Finally, for cases where two or more distinct peaks were identified on an individual sample, the true peak was assumed to be the peak which occurred at the same time as peaks on other samples with no interference. Examples of peak interpretations are available in B. Chromatograph Interpretation.

To verify quality control sample assays also included blanks, spikes, and splits. Depending on the number of samples in a given HPLC run, “blank” vials containing DI water were interspersed every 3-5 samples to ensure there was no delayed sample elution or residual contaminant in the column. Similarly, high concentration controls of CBZ or DCF would sometimes be put in place of blanks to ensure concentrations were being measured accurately, and that concentrations of one sample would not interfere with the following sample. Samples collected from isotherms and column trials were regularly collected in duplicate or triplicate at the same time to measure precision through splits.

4. RESULTS

This section presents the results of experimentation at the three different scales and preliminary comparisons between them.

4.1 Adsorption Isotherms

Results across the six isotherm experiments produced generally consistent results, where both CBZ and DCF showed a significant increase in adsorption capacity in all models as organic content increased in the soils. Doubling the SOC between the medium and high organic soils, CBZ adsorption increased by two orders of magnitude, and DCF increased by one order of magnitude. This outcome is consistent with expectations, which link greater adsorption of organic compounds to higher organic content of the soil.

These results are summarized in Table 4, which lists the calculated K values for each model in each experiment, and the associated RMSE for each model, with the best fit for each experiment emphasized in bold text. K values are presented for each model, but additional terms of the Freundlich and Langmuir isotherms are excluded as they are only present in their respective models. It should be noted that the units of K_d for the linear model and K_F for the Freundlich model are in units of (L/g), while the Langmuir K_L value is in units of (mg/g), making it difficult to directly compare these values.

Table 4: Summary of findings across the isotherm experiments

		Carbamazepine		Diclofenac	
		K_n Value	RMSE	K_n Value	RMSE
Sand	Linear (K_d)	7.00 x 10^{-4} (L/g)	2.76 x 10^{-3}	9.00 x 10^{-5} (L/g)	9.84 x 10^{-3}
	Langmuir (K_L)	-1.18 x 10^{-2} (mg/g)	8.51 x 10^{-3}	-1.42 x 10^{2} (mg/g)	1.36 x 10^{-2}
	Freundlich (K_F)	**1.70x10^{-4} (L/g)**	**6.50 x 10^{-4}**	**8.28 x 10^{-6} (L/g)**	**1.15 x 10^{-3}**
Medium Organics	Linear (K_d)	5.00 x 10^{-3} (L/g)	1.14 x 10^{-2}	4.50 x 10^{-3} (L/g)	1.37 x 10^{-2}
	Langmuir (K_L)	3.55 x 10^{-1} (mg/g)	1.12 x 10^{-2}	1.75 x 10^{0} (mg/g)	1.19 x 10^{-2}
	Freundlich (K_F)	**1.57 x 10^{-2} (L/g)**	**2.67 x 10^{-3}**	**2.57 x 10^{-2} (L/g)**	**6.87 x 10^{-3}**
High Organics	Linear (K_d)	9.70 x 10^{-3} (L/g)	3.08 x 10^{-2}	8.10 x 10^{-3} (L/g)	2.13 x 10^{-2}
	Langmuir (K_L)	4.40 x 10^{0} (mg/g)	1.75 x 10^{-2}	8.89 x 10^{0} (mg/g)	1.77 x 10^{-2}
	Freundlich (K_F)	**4.17 x 10^{-2} (L/g)**	**1.25 x 10^{-2}**	**3.85 x 10^{-2} (L/g)**	**3.04 x 10^{-3}**

An example of the model-fit plots generated for each experiment is shown in Figure 11, where the equilibrium concentration of CBZ is plotted on the x-axis and equilibrium adsorption in medium-organic soil on the y-axis. While the best-fit model was determined for each experiment by comparing R^2 and RMSE values, these plots were valuable to visualize each model's fit for each experiment. R^2 values were determined from linearized forms of the Langmuir and Freundlich models, while RMSE values were calculated using the true model and observed data, so the RMSE was considered to be the more important parameter in cases where R^2 and RMSE did not agree. Plots were produced for all six experiments and are included in D. Isotherm Model Fits, with one representative plot presented here (Figure 11).

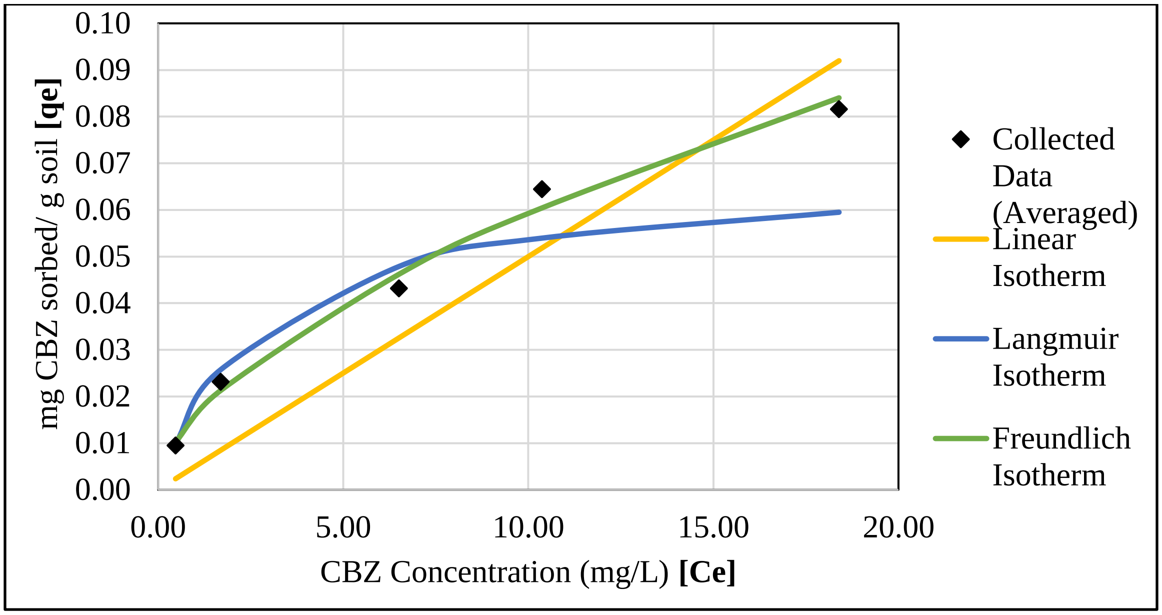


Figure 11: Isotherm model-fit plots for Linear, Langmuir, and Freundlich isotherms for CBZ in medium organic soil

For all six experiments, data produced a reasonable fit to all three isotherm models, with the exception of a Langmuir fit in the DCF-Sand isotherm. In all cases, the Freundlich model was the best fit. Parameters of the Freundlich isotherm for each experimental condition are summarized in Table 5, where K_F is the adsorption capacity and n is the adsorption intensity (Equation 3a, 3b)

Table 5: Freundlich Isotherm Parameters Across Experiments

Condition		K_F (L/g)	n
Sand	CBZ	1.70×10^{-4}	0.73
	DCF	8.28×10^{-6}	0.64
Medium Organics	CBZ	1.57×10^{-2}	1.74
	DCF	2.57×10^{-2}	2.79
High Organics	CBZ	4.17×10^{-2}	2.31
	DCF	3.85×10^{-2}	3.00

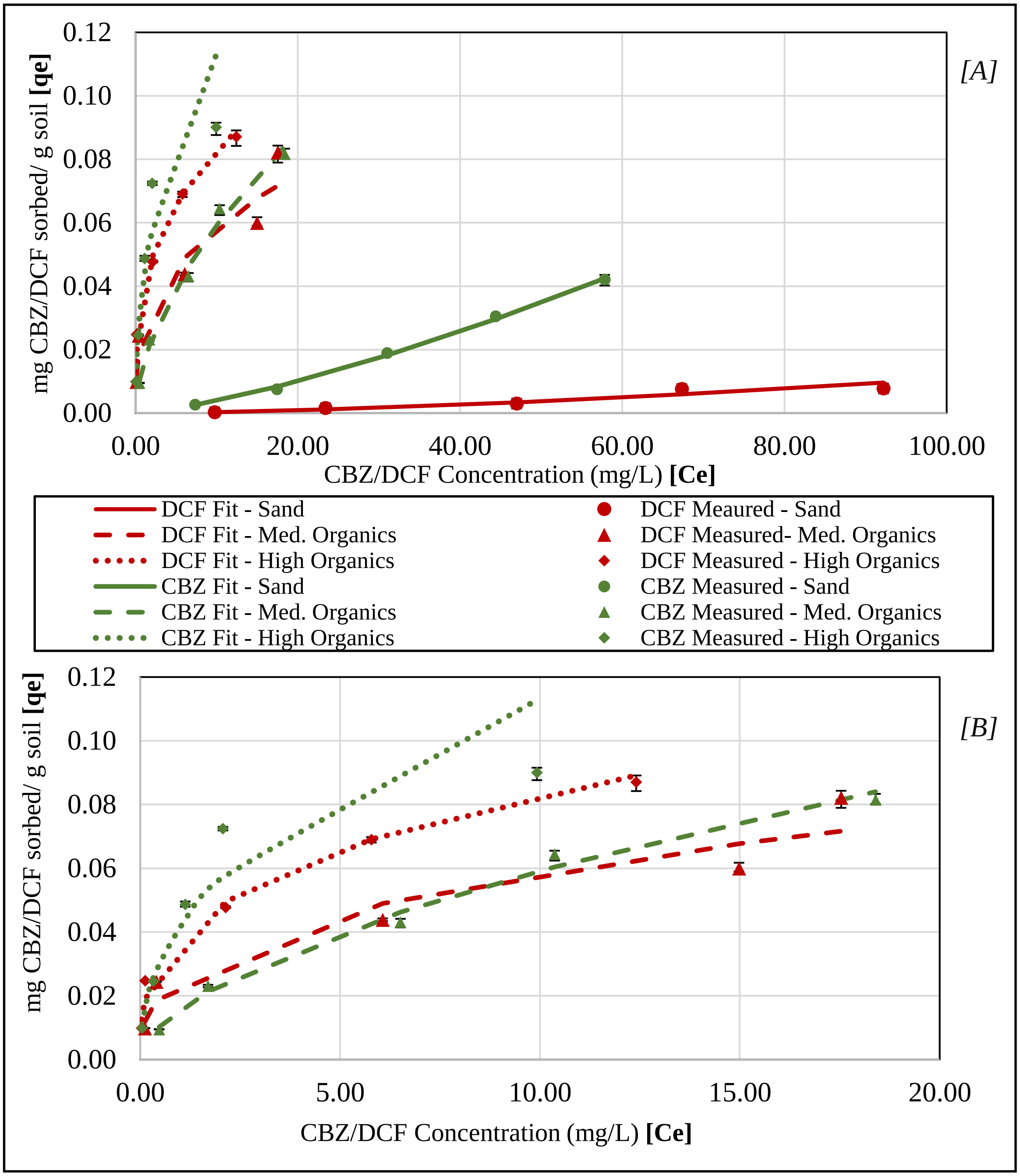


Figure 12: Effect of soil organic content on CBZ/DCF adsorption isotherms

Lines indicate a smoothed fit of the Freundlich model under each condition. Averaged values of measurements are presented as points. Bars on each point indicate the measured range of values across the three samples at each value. [A] shows the results across all experiments, while [B] shows the same plotted data but excludes the sand isotherms to show better detail of the organic soils fit.

Results of this experiment showed a clear correlation between the organic content of a soil and the amount of CBZ/DCF adsorbed. Figure 12 shows the equilibrium concentrations of CBZ and DCF are lowest in the high organic soil across all starting concentrations, with the exception of the 10 mg/L starting concentration which was essentially fully adsorbed by both medium and high organic soils. Similarly, the sand with no organic content was shown to have a substantially weaker effect on adsorption than organic soils. Equilibrium concentrations were higher across both trials in sand for all starting concentrations, and q_e was lowest in all cases. In sand and high organic soil, more CBZ was adsorbed than DCF for all initial concentrations. In medium organic soils there was only a slight distinction between CBZ and DCF adsorption, where slightly more DCF was adsorbed for initial concentrations up to 50 mg/L CBZ/DCF and slightly more CBZ was adsorbed at higher initial concentrations.

4.2 Bench Scale Column Results

Results of bench scale soil column experiments showed a trend of organic soils having a higher adsorptive capacity than sand, shown by later breakthrough times. Results also indicate that CBZ adsorbs more than DCF under these experimental conditions (Figure 13). These results are generally consistent with the isotherm results.

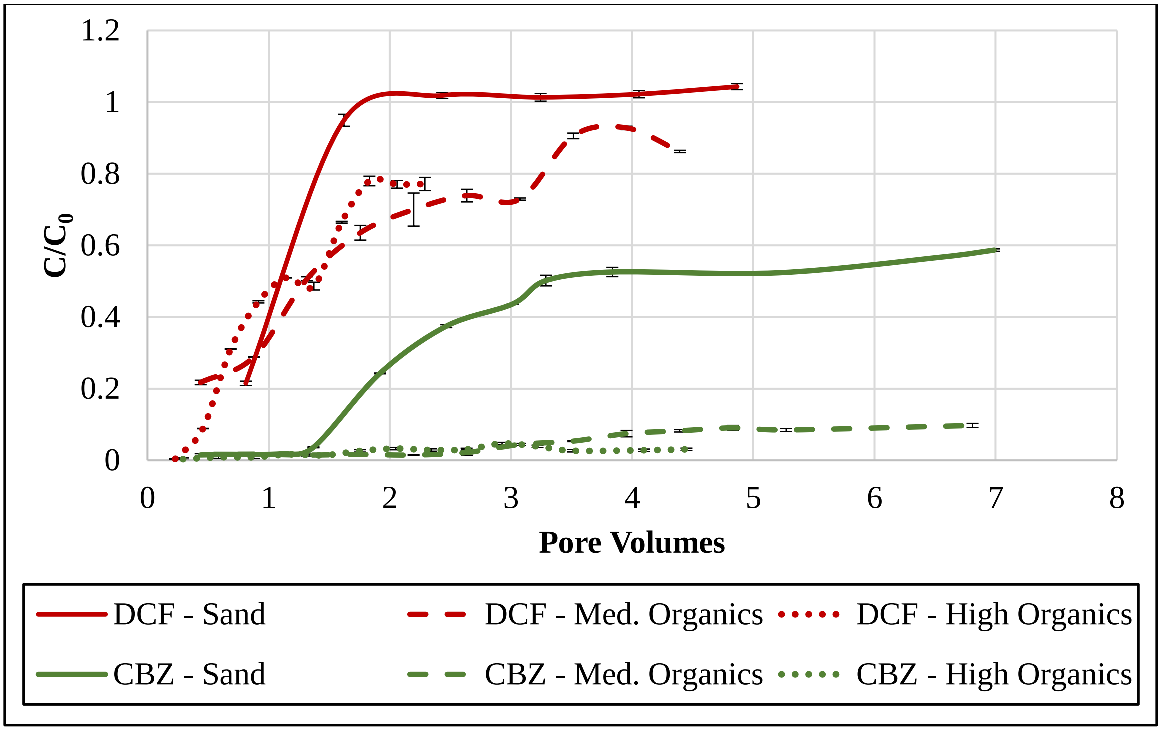


Figure 13: Results of bench column trials

Breakthrough behavior was observed in all soils for both contaminants, but significantly more CBZ was retained by the soil than DCF. Table 6 shows the experimental conditions for each trial, including the soil porosity and the volume of effluent passed through each column.

Table 6: Experimental Properties of Bench Columns

		Soil Volume (cm^3)	Pore Volume (cm^3)	Porosity After Saturation (n)	Influent Added mL	Influent Added Pore Volumes
DCF	Sand	903	123	0.13	600	4.87
	Med. Organic	1302	228	0.17	1600	7.03
	High Organic	1774	437	0.25	1800	4.12
CBZ	Sand	844	109	0.13	800	7.31
	Med. Organic	1252	228	0.18	1500	6.59
	High Organic	1644	342	0.21	1700	4.98

4.2.1 CBZ

Through the first 1.5 pore volumes, all soils appeared to retain the majority (~99%) of CBZ in the influent. Past this point, effluent concentrations steadily increased in the sand up to ~53% of initial concentration by four pore volumes, then gradually increasing up to seven pore volumes with an ultimate relative concentration of 59%. Effluent concentrations of CBZ in medium organic soil only appeared to increase around 2.5 pore volumes at a slightly greater rate than high organic soil, but substantially less than the sand. By six pore volumes, effluent concentration in sand was roughly 9 times greater than concentration in the medium organic soil. CBZ concentration in high organic soil began increasing around 1.5 pore volumes as well but much more gradually than in the sand; by 2.6 pore volumes the effluent concentration was only 3% of the initial concentration.

4.2.2 DCF

In sand, DCF appeared to reach full breakthrough within two pore volumes, with effluent concentration remaining essentially equal to initial concertation beyond that point. By this same point (two pore volumes) effluent concentration in medium organic soil was approximately 68% of initial concentration, and in high organic soil it was around 77% of initial concentration. Ultimate C/C_0 values for sand, medium organic, and high organic were 100%, 86%, and 77%, respectively, although pore volumes passed were not equal at this point. In an attempt to extend the breakthrough curves for organic soil more DCF solution was passed through the columns two days later, but results were not consistent (discussed further in section 7.2 Additional Areas of Study).

4.3 Large Scale Column Results

Results of large-scale column experiments yielded largely inconclusive data (Figure 14). Due to time constraints, large-scale experiments could not be repeated, so results shown below are presented more for discussion rather than conclusions, although some trials of the experiment did yield valuable data.

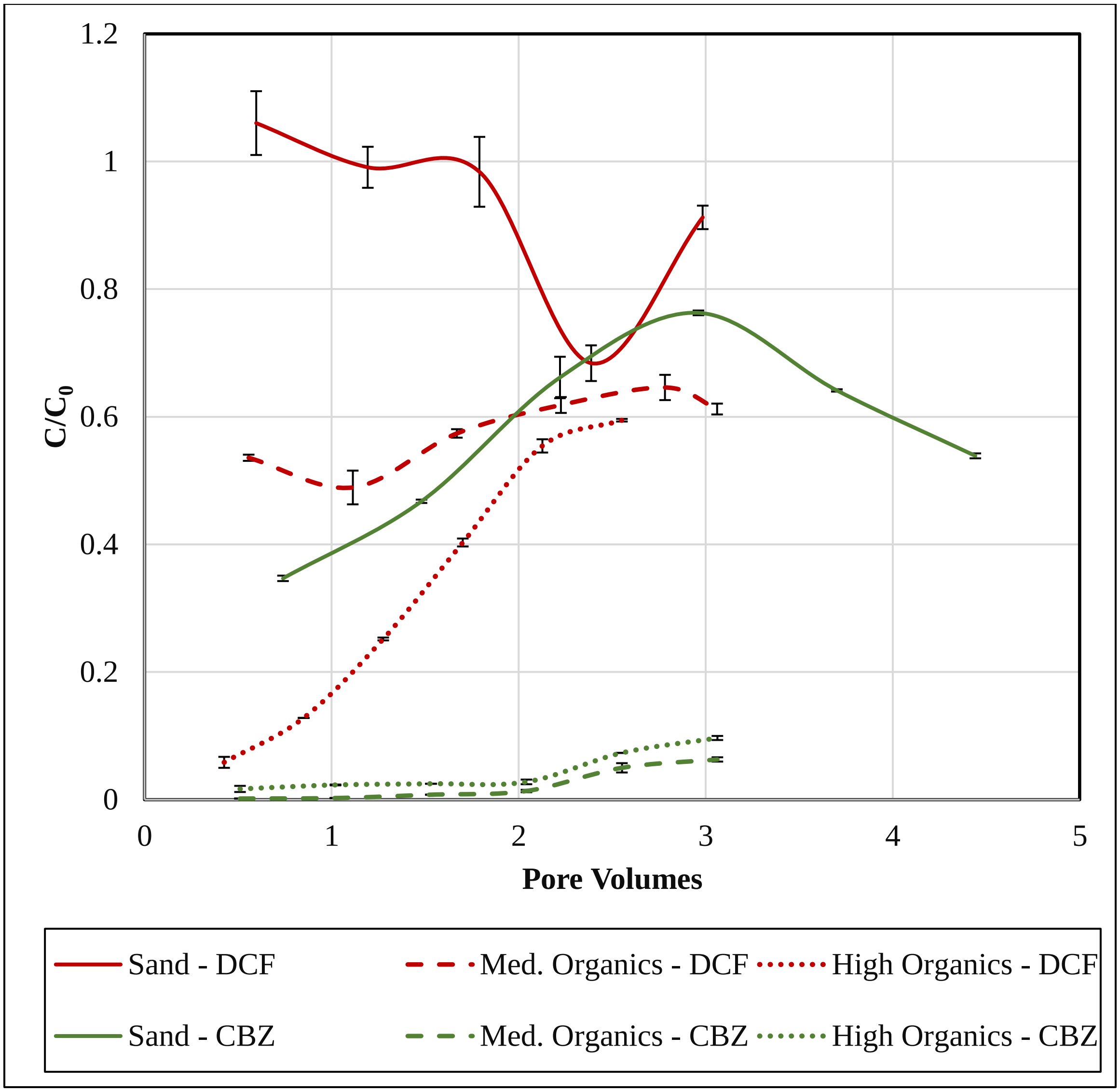


Figure 14: Summarized Results of Large Column Experiments

For both CBZ and DCF in sand columns values appeared to oscillate inconsistently showing no clear indication of breakthrough. A similar trend was observed in the medium organic soil with DCF. Medium organic soil retained almost all of the CBZ for the first two pore volumes, then concentration appeared to start increasing as expected in a breakthrough curve. High organic soil showed high initial adsorption of both DCF and CBZ, but DCF increased in concentration much quicker than the CBZ. CBZ in high organic soil was almost completely adsorbed (~98%) for the first two pore volumes, then began to increase. Medium organic soil appeared to retain more CBZ than the high organic soil within the same amount of measured pore volumes, though these results are too similar to be definitive. This oscillatory behavior may be explained by incompletely saturated soil columns, which contained air bubbles in soil pore space at the start of the experiment.

5. DISCUSSION

This section expands upon the findings presented in the results section to identify relationships, contextualize data, and discuss potential sources of error and experimental limitations.

5.1 Findings Across Experiments

5.1.1 Comparing PPCP Behavior Across Scales

A key goal of this study was to explore the consistency of findings across experimental scales. Consistency here refers not only to the behavior of a single PPCP at different experimental scales, but to see if these trends are consistent for different PPCPs with different physiochemical properties. Findings of this study support the idea that general trends with different contaminants are consistent across varying experimental scale, despite physiochemical differences between CBZ and DCF. The nature of the different experiments presented in this study prevents a direct quantitative comparison of findings across scales, however Table 7 allows for a semi-quantitative comparison.

Table 7: Comparison of adsorptive behavior across experiments

Condition		Isotherms		
		Adsorption Capacity K_F (L/g)	Lowest C/C_0	Initial Concentration with Greatest Reduction (mg/L)
CBZ	Sand	1.70×10^{-4}	0.58	100
	Medium Organic	1.57×10^{-2}	0.07	10
	High Organic	4.17×10^{-2}	0.01	10
DCF	Sand	8.28×10^{-6}	0.90	75
	Medium Organic	2.57×10^{-2}	0.01	10
	High Organic	3.85×10^{-2}	0.00	10

Condition		Bench Columns		Large Columns	
		C/C_0 at Plateau Start	Pore Volumes at Plateau Start	Final C/C_0	Final Pore Volume
CBZ	Sand	0.53	3.83	*	*
	Medium Organic	0.09	4.83	0.06	3.06
	High Organic	0.03	4.45	0.09	3.06
DCF	Sand	1.00	2.00	*	*
	Medium Organic	0.91	3.50	0.61	3.06
	High Organic	0.78	1.80	0.59	2.55

Values for sand columns in the large columns are excluded due to inconsistent results

Table 7 shows a point which was chosen as the most representative of results of each experimental condition in the three experiments. For the isotherms, the point which showed the greatest reduction in concentration from the initial concentration was chosen; the change in concentration and respective initial concentration are presented, along with the Freundlich adsorption capacity calculated for that experiment. For the bench columns, the point closest to the start of a visual plateau in the breakthrough curves was chosen. In the absence of a distinct plateau, the ultimate PV was used instead. For the large columns, the point at the highest PV of each curve was chosen, and sand columns were excluded due to their inconsistent results. These results are presented together here only to allow a precursory comparison of findings across all experiments, but results of adsorption isotherms are generally used to predict behavior of column experiments and not to be directly compared (Onesios and Bouwer 2012).

The following conclusions are presented without distinction between CBZ or DCF to emphasize the conclusions drawn about experimental scale. Again, these trends are consistent for both contaminants. When the effluent-soil system is allowed to reach equilibrium as seen in the isotherms, organic soils are able to remove substantially more contaminant from the liquid phase than sand, and high organic soil removed more than medium organic soil. As the SOC increases in the adsorption isotherms, the adsorption capacity (K_F) increases, and the maximum removal in the isotherms increases as well. If the soil columns and isotherms behaved identically, the PPCP-Soil systems with higher K_F values should be expected to breakthrough later than the systems characterized by a lower K_F value. With the possible exception of DCF-Sand in the bench columns, soil columns did not reach complete breakthrough (C/C_0=1.0) within the duration of the presented experiments. Results between medium and high organic soils were not always distinct, however, it was found that across all experimental scales that significantly more adsorption occurs in organic soil when compared to sand. However, these results cannot make a definitive statement that increasing SOC in an organic soil increases adsorption in a non-equilibrium setting such as soil columns. In both bench columns and large columns, several points show a higher outgoing concentration in high organic soils than medium organic soils, especially when considering the margins of error at each point. While the points chosen in Table 7 do show a lower concentration in high organic soils than in medium organic soils, the PVs are lower in the high organic soils than medium organic soils for most points. A lower PV effectively means less effluent has passed through the soil relative to the total volume of soil, which can be related to the specific surface area of the soil. Adsorption is a surface-mediated process, so PVs can be used to compare behavior between soils with different porosities, or experiments with different masses of soil. A comparable C/C_0 at a lower PV may indicate that adsorption occurring less in the higher organic soil. These findings reinforce the conclusions of this study, that only general trends (i.e. EC behavior in organic vs inorganic soils) are consistent across experimental scales, whereas more refined trends (i.e. EC behavior in medium vs high organic soils) may present inconsistencies across experimental scales. This inability to confidently assess more refined trends across experimental scales in non-equilibrium states may stem from decreased experimental control in larger scale experiments increasing error, as explored in the following section, or it may be indicative of more complex physiochemical or pharmacokinetic interactions which are affected by scale.

5.1.2 Isotherms

Values of the partition coefficient “K” varied substantially cross different models for the same experimental conditions. Because the linear, Langmuir, and Freundlich isotherms are derived differently it is difficult to directly compare units of K due to the presence of other dimensionless constants. Across all experiments however, the Freundlich isotherm was found to be the best fit between the three utilized models.

This finding corresponds to expectations based on the methodology of the Freundlich isotherm. This is an empirical model which primarily diverges from the derived Langmuir model through the assumption of heterogenous media. Adsorption is determined by the adsorption energy (ΔH) of a given sorbate/sorbent system; the Langmuir model is derived under the assumption that all sorbent material has the same ΔH value, while the Freundlich assumes that the ΔH value varies across bulk sorbent material. All three soil types utilized here can be characterized as heterogenous material. The organic blended soils are heterogenous by definition; they are composed of a heterogenous mixture of the concrete sand and organic topsoil. The topsoil is assumed to be composed of a mixture of lignin, or woody material, and organically derived humic substances. The concrete sand may be more homogenous than the topsoil, but it still possesses a degree of heterogeneity; while the bulk of the substance appears to consist of silica sand, a visual inspection of it also reveals the presence of other solid matter used in the mixture (Figure 15). Colors of particles range from dark yellow to red to white. This may be explained by a presence of distinct types of rock or aggregates like brick, or it may simply indicate sand grains exposed to varying degrees of oxidation or weathering. Grain morphologies range from subrounded to angular, and grain sizes are visibly heterogeneous. Regardless, it can be assumed that chemical and morphological differences between surfaces of these particles may result in chemically heterogeneous behavior.

Figure 15: Visible heterogeneity in sand

A variety of sizes, shapes, colors, and degrees of clarity in grains suggests variable mineralogy and oxidation.

This experiment occurred in the most controlled conditions of the three experiments in this thesis; unsurprisingly this led to the most consistent results across experimental conditions. At this scale, the mass of soil down to 1μg was recorded. Because each isotherm experiment required five solutions of variable concentrations, fresh solutions were prepared for each of the six experiments which were also used to create calibration curves. Fresh solutions were prepared for column experiments as well, but because they were conducted all at a single concentration of 30 mg/L, calibration curves could not be created for individual column experiments, so calibration curves from isotherm experiments were used as reference.

For both contaminants, results were consistent with accepted findings that increasing SOC increases the adsorptive capacity for a given mass of soil (Chefetz et al. 2008) (Ilyas et al. 2021). Lower initial concentrations of contaminant (10mg/L, 25mg/L) showed similar degrees of adsorption for both contaminants, but at higher initial concentrations a greater amount of CBZ or DCF was removed in all soils.

An important caveat to these results is that the Freundlich fit can only be confidently stated as the best fit at these concentrations; experimental concentrations here are 100x-1000x higher than typical environmental conditions. The Langmuir model can be ruled out as a better fit at lower concentrations due to its assumption of a maximum adsorption capacity which was not observed at higher concentrations presented here. At concentrations higher than reported in this experiment, it is possible that asymptotic behavior may develop and indicate the Langmuir is a better fit for higher concentrations. At lower concentrations, adsorption behavior may be better fit to a linear model, or one of the other less common adsorption models detailed in (Juela et al. 2021).

5.1.3 Bench Columns

The bench columns allowed for exploration of CBZ/DCF fate in a flowing system more representative of SAT than adsorption isotherms while still allowing for a good degree of control. Breakthrough behavior was observed in all soils for both CBZ and DCF to at least some degree. As suspected, the sand demonstrated significantly less adsorption than organic soils for both drugs. Results of the bench column experiments diverged from findings of the adsorption isotherm experiments, where the bench columns showed substantially more adsorption of CBZ than DCF across all soils. In isotherm experiments more CBZ was adsorbed than DCF for most points, but the disparities were less pronounced. A possible explanation may relate to the polarity of these substances, because CBZ is a polar substance it may display a greater affinity for negatively charged surfaces of clay particles in soils. (Silver et al. 2018) and (Chefetz et al. 2008) also found that CBZ was adsorbed more than DCF in similar soil columns. While there is overlap in the accepted ranges of log K_{OW} between CBZ and DCF, the latter is generally reported as having a higher value indicating greater lipophilicity. Increased lipophilicity is associated with increased affinity in adsorption to organic matter, so if this were the controlling variable greater adsorption of DCF than CBZ would be observed in organic soils. This disconnect indicates that pharmacokinetics of these drugs requires more focused investigations on their behaviors in soils, which is well beyond the scope of this study.

Of the six presented breakthrough curves, three appear to display “shoulders” in the curves, or data points where C/C_0 was more or less the same as the previous reading resulting in a flat or slightly dipping section of the curves. Lacking a better physical explanation of this behavior, which was not described in other literature using soil column studies, this behavior is most likely the result of analytical variability in the HPLC. In sand C/C_0 reached a value of ~1.0 in roughly two pore volumes for DCF, by three pore volumes CBZ also reached a somewhat constant value, however it was at C/C_0 in the range of 0.55-0.6 indicating that adsorption was still occurring, but the rate at which it changed was almost constant. This may indicate a kind of pseudo-equilibrium, where rates of adsorption and desorption became almost equal, although the concentration begins to gradually increase again around six pore volumes. This behavior appeared in some studies which produced CBZ breakthrough curves (Silver et al. 2018), but not observed consistently (Williams et al. 2014), suggesting this behavior may only be present in some soils.

Interestingly, for the DCF breakthrough curves for the medium versus high organic soil showed more adsorption, at least initially, in the medium organic soil than the high organic soil, contradicting findings of the isotherms. A possible explanation of this would be the unintended effect of increasing irregularity in the soil system as organic content increased. The topsoil blend used for controlled SOC in soil blends contained a large fraction of elongated woody material which may have increased the potential for preferential flowpaths to develop in bulk soil matter with increased topsoil content. Because this asymmetrical material inhibits the close packing structure expected in granular soils, effluent may have followed irregular or biased flowpaths through these soils. Essentially if such irregularities did occur, some regions of the soil may have passed a majority of the effluent, while others had less contact with the effluent. It is also possible that all regions of the soil passed the same volume, but interstitial velocity may have been greater in some regions resulting in reduced contact time and therefore less adsorption potential. If either or both of these processes occurred, it may explain why medium organic soil showed increased adsorption capacity of flowing effluent when compared to isotherm results, where such irregularities in flow could not occur.

5.1.4 Full Columns

The full columns represent the experiment with the least amount of control, which is reflected in the results. While confidence in the findings of this experiment is less than in the adsorption isotherms or bench columns, some conclusions can still be drawn.

Behavior of both contaminants in sand was irregular, and findings were ultimately inconclusive. For the DCF in medium organic soil, if the first point of Figure 14 is excluded, a slight increase in concentration is observed over the rest of the curve, indicating possible breakthrough behavior if more data were collected. The first data point is still nearly half of the initial concentration, substantially greater than readings at similar pore volume in the bench columns. Across the length of the curves, outgoing concentration of CBZ was higher in the high organic soil than in the medium organic soil. This may be a result of the suspected increase in physical irregularity mentioned in Section 5.1.3 Bench Columns the rate of discharge was significantly higher in the high organic soil which results in decreased contact time with the soil. Any disparities between results of adsorption isotherm experiments and bench column experiments are assumed to be augmented in the large columns as the experimental conditions become increasingly variable in larger scale experiments.

5.2 Identified Sources of Error

5.2.1 General Experimental Errors

Figure 16: Difficulties in measuring gradation of organic mixed soils

Chosen methods to control SOC had significant drawbacks in experiments. While a store-bought topsoil had the benefit of a readily available source of organic material, geotechnical analysis of the blended soils quickly revealed a flaw. Organic matter in commercial topsoil is largely present as woody or mulchy substrate. This may not be an accurate representation of organic matter in sub-surface soils, which have experienced much more weathering leading to less irregularity in particle morphology. These results also affected the characterization of soil grading – to pass through a standard sieve, a given particle only needs to have 1-dimension smaller than sieve openings to pass through. Figure 16 shows an example of irregularity (elongation, asymmetry) in woody particles, which only need to fit through a sieve in 1-dimension. While a sand particle is roughly uniform in all dimensions at this size, these woody particles have lengths at least an order of magnitude greater than their widths. These morphological irregularities also affected the flow regime of the blended organic soils in column trials. Such elongate particles are not conducive to tight packing in a bulk soil and introduce pathways for water to flow through much quicker than intended. In the full column studies, discharge of the high-organics soil was nearly double that of the sand column.

5.2.2 Errors in Adsorption Isotherms

This was the most controlled experiment of the three conducted and did not yield any immediately identifiable sources of error. It would be more accurate however to have maintained a constant temperature across all experiments.

5.2.3 Errors in Bench Scale column experiments

An undetermined factor led to the flow rate through the sand columns for CBZ to be significantly slower than any other bench column experiment. The problem persisted after attempting to use a different column, washing the column filter with methanol, and adding the sand in small (~50g) increments instead of large volumes like the other columns. Results of this experiment did not show any unusual behavior, but it may have been the result of a limited number of small channels forming in the soil which could reduce effective surface area and lead to increased breakthrough.

5.2.4 Errors in Large Scale Column Experiments

Substantial errors were present in this experiment as indicated by the largely unproductive results shown in Figure 14. The most immediately visible error was the lack of data. Due to campus environmental health and safety (EH&S) regulations, these experiments were limited by the amount of liquid waste generated. For each experiment only two 55-gallon waste drums were provided which meant only 110 gallons of CBZ/DCF solution could be pumped through the columns. Given the size of the columns and the nature of the soils within them, this limited data to only 3-5 estimated pore volumes pumped through each column. Furthermore, concentrations of the CBZ/DCF solution fed into the columns was also not able to be kept consistent. While the inside of the 55-gallon feed barrel was marked with tape to indicate volume, these measurements were not precise and it was difficult to have identical volumes of water leading to inconsistent feed concentrations. Because the water used to fill these drums was from a hose used for concrete work and not filtered DI water, it is presumed that mineral impurities in the water may have caused precipitation of CBZ or DCF which altered concentrations between refills. For the CBZ trials, the initially clear solution of dissolved CBZ became an opaque white when added to the hose water at first.

5.3 Limitations

Due to analytical limitations, experiments were conducted here at concentration several orders of magnitude greater than environmental concentrations. Environmental concentrations of CBZ and DCF are most typically in the range of ng/L (Aydın et al. 2021). At the start of the experiment, trials were conducted at concentrations closer to

reported values, generally in the μg/L range. Despite refining processing methods in the HPLC however, at such low concentrations it became too difficult to distinguish signals from noise in chromatographs. A method detection limit (MDL) of approximately 1 mg/L for both CBZ and DCF was determined, which meant the experimental concentrations had to be reassessed. Initial concentrations of experimental solutions ranged from 10 mg/L to 100 mg/L so that a minimum of 90% reduction of concentration could be reliably identified in data. While this led to relatively consistent results, it makes it difficult to directly apply these findings to environmental applications.
For example, the Langmuir adsorption model is dependent on the parameter q_m which is associated with the maximum adsorption capacity in a measured system. Due to the elevated concentration of contaminants in this study, this maximum value was reached more quickly than in a SAT study capable of measuring environmental concentrations. Similarly, breakthrough was likely achieved in fewer pore volumes than in an experiment at environmental levels.

A possible explanation as to why CBZ was shown to adsorb more than DCF in this thesis and other studies such as Silver et al. (2018) and Chefetz et al. (2008) was that it may be attracted to negatively charged surfaces of clay particles. In order to determine the amount of clay present in the soils of this thesis, a fines analysis such as ASTM D7928 could have been conducted to determine this was an influence or not.

Other studies reviewed (Silver et al. 2018) (Benotti et al. 2009) (Kwon and Rodriguez 2014) utilized a HPLC-MS system, a more refined HPLC with additional mass spectroscopy capabilities. These are capable of more precise analysis of specific compounds, like DCF or CBZ, in complex media allowing for accurate measurements closer to environmental concentrations. HPLC-MS is also better suited to identifying specific compounds, because traditional HPLC is an indirect measurement of absorbance at a chosen wavelength. This experiment saw several false peaks in samples collected in the organic soils, which were presumably caused by other soluble compounds present in the soil. These samples required a more subjective determination of target compound concentrations. Quality analysis and control could be improved for experiments in this study if the effluent from passing water through the soil columns was collected and analyzed before the addition of CBZ or DCF in order to determine how soluble soil compounds influenced chromatographs. Additionally, if clean water was continually run through the columns and effluent was regularly sampled, HPLC results could reveal whether the concentration of these soluble compounds was decreasing as more fluid is eluted. This would serve to identify any potential background interference with the CBZ/DCF solution from the soil matrix.

If soil columns were saturated by adding water from the bottom of the columns instead of the top, there would have been fewer air bubbles present in soil pores, which may have caused occlusion of flow in the large columns as mentioned in Section 5.1.4 Full Columns

Initially, this study aimed to provide a more quantitative comparison of findings across isotherm and column experiments, but ultimately this was not possible under these experimental conditions. Studies such as (Juela et al. 2021) suggest numerical models capable of this, but utilize equilibrium models which could not be derived here. Such models require precise measurements of constant discharges and timing in experiments which was not possible here. Complexities also arise in the comparisons of equilibrium and non-equilibrium states as seen between the isotherm and column experiments. Due to analytical limitations and a need for complex mathematical derivations (Poursaeidesfahani et al. 2019), a robust quantitative comparison of isotherm and column experiments was beyond the scope of this study.

6. CONCLUSIONS

The goal of this study was to determine the consistency of results across three experimental scales for common PPCP soprtion experiments which can be used to support SAT feasibility. Ultimately, this study shows that there is a degree of consistency across different scales for broad trends. Small, medium, and large-scale experiments consistently showed that organic soils express increased adsorption capacity in comparison to an inorganic sand, and that CBZ is adsorbed more than DCF. More refined trends were less consistent across scales however. Most experiments showed higher adsorption in high organic soils, but some showed higher adsorption in medium organic soils. It is generally accepted that increasing SOC increases the adsorption capacity of soils, so the data showing higher adsorption in medium organic soil could be the result of experimental error, or by the variability of non-equilibrium systems. Because consistency across scales was the focus of this study and not specifically the effect of SOC on PPCP adsorption, such findings which are seemingly inconsistent with expected behaviors provide valuable insight into the effects of experimental scale.

In practice there is an inverse relationship between the physical scale of an experiment and the degree of control over the experiment. At the smallest experimental scales of this experiment, soils were sterilized, identical volumes of effluent were used, and the entire soil-effluent system could be viewed from any angle. While it would be technically possible to conduct these control procedures for all of the soil in a large column or pilot-scale SAT experiment, it would be impractical. At larger scales, assumptions and generalizations must be made. Porosity of one or two samples from a large study must be used to estimate the bulk porosity of a soil. Flow can be assumed as homogenous, but soil is an intrinsically heterogenous media, so such assumptions are bound to cause discrepancies between expected and measured results. Taking a soil sample from a potential SAT site for laboratory analysis will inexorably disturb its natural structure, which can affect how water flows through it and ultimately the behavior of a target compound in solution. The results of this study make such conclusions abundantly clear – laboratory investigations of complex physiochemical behavior in a heterogenous media will vary from natural conditions, and results are likely to vary as the degree of control over an experiment varies.

Beyond the decrease in experimental control, another critical factor may contribute to the unexpected behavior in the soil columns when compared to the isotherms. The purpose of adsorption isotherm experiments is to determine the concentrations of target compounds in the mobile phase when a system is in equilibrium. Because soil column experiments are not in equilibrium, they can not be expected to behave the same as experiments occurring at equilibrium. Even when a breakthrough point of $C/C_0 = 1.0$ is reached, soil columns are not necessarily in equilibrium. Influent is continually passing through these systems carrying out not only the dissolved target compound, but also other soluble soil compounds and fine particulate matter. This contributes to the difficulty in making direct comparisons between adsorption isotherms and larger non-equilibrium soil columns, and emphasizes the importance of understanding the effects that different types and scales of adsorption experiments can have on data trends. Because these experiments are being used to predict behavior in full-scale SAT sites, such trends then affect the ability to draw conclusions about real-world performance from laboratory experiments. In a thesis focusing on the effects of experimental scale on the adsorption of PPCPs in soils, it may have been inaccurate to consider the isotherms a “small” experiment and compare to bench and large scale soil columns. These kinds of experiments are fundamentally different, and the isotherm results should be used to inform and contextualize column results, not serve as a direct comparison.

Additionally, this study focused only on the adsorption of PPCPs, or their partitioning from a dissolved liquid phase to a solid phase on soil surfaces. This is a crucial factor to understanding SAT performance but is only one aspect of performance. Once adsorbed to a soil PPCPs can either be degraded through chemical or biological processes, or they can desorb and remobilize in the environment. To benefit water quality, SAT must not only remove PPCPs from the dissolved phase, but also degrade these compounds so they do not persist in the environment. Thus, the findings of this study on the effects of scale on PPCP adsorption can not be fully applied to SAT performance without validation that similar trends are also identified on the biological and chemical degradation of adsorbed PPCPs.

Despite the inevitable variabilities between experiments, the major trends in PPCP adsorption behavior do not appear to change across experimental scales. The goal of this study was not to determine the exact behavior of a hypothetical SAT system, but to determine if broad trends seen in simple laboratory experiments may be consistent with larger more involved studies of SAT site feasibility. Because these broad trends were shown to be consistent across experimental scales it is inferred that small-scale experiments such as adsorption isotherms can be used in the preliminary assessment of SAT site feasibility. Lack of consistency in more refined trends, such as varying organic content in an organic soil, indicate that such experiments are not viable as a replacement of comprehensive investigations of SAT performance once a site has been determined.

7. FUTURE WORK

Proposed future work can be split into two categories: increasing accuracy of experiments conducted here, and experiments exploring other factors not considered for these experiments.

7.1 Improving This Study

As previously mentioned, this experiment was unable to make accurate measurements at the environmentally-relevant concentrations of CBZ/DCF. This would be possible through utilization of more sensitive analytical methods such as using an HPLC-MS in place of the HPLC. It may also be interesting to conduct these experiments with actual tertiary WWTP effluent instead of the synthetic CBZ/DCF "influent" used here. This may give insight into how competition for adsorption sites affects the removal of PPCPs when multiple contaminants are present in the experimental solution. Furthermore, to better understand the effects of organic content in a system of effluent flowing through soil (bench columns, large columns), a soil more typical of an actual SAT system may yield more applicable findings. Natural soils with medium and high organic contents should be used in place of the synthetic Sand/Topsoil blends. If this is not feasible, the topsoil could be processed or milled to reduce potential preferential flow paths related to the elongation and asymmetry observed in woody matter. For soils used in this thesis, further characterizations may have also benefitted experimental conclusions. Analyses of soil clay content or fine content could support or oppose the idea that negatively charged clay particle surfaces displayed an affinity for polar CBZ. Additionally, if hydraulic conductivity and tortuosity analyses were conducted, better analyses of how a fluid flows through the soil would make it easier to facilitate a constant EBCT across experiments.

The large-scale column experiment could be improved as well. Through better coordination with campus EH&S, a better hazardous waste management system could be devised allowing for the experiments to be conducted for longer and producing more representative breakthrough curves. Use of filtered water to prepare feed solutions in place of industrial water from a hose may also improve the accuracy of measurements by preventing coprecipitation. To ensure consistency of initial concentrations of feed effluent, a better system of taking large volumetric measurements could be devised as well. A variable flow pump could also be beneficial to the experiment to match pump discharge to column discharge allowing for continuous infiltration without ponding affecting the hydraulic gradient. Because this thesis aimed to compare results of similar experiments at different scales, controlling the influent discharge rate to yield a consistent EBCT for all column experiments would remove a degree of uncertainty on effects of scale on these experiments. By maintaining relatively consistent residence times and pore water velocities, effects of scale on adsorption will be easier to distinguish from other phenomena.

In order to determine whether the irregularities in soil packing were causing preferential pathways for flow to develop, bench and large scale column experiments would both benefit from a non-reactive tracer study in the columns. A tracer study in the columns may reveal where advection or dispersion are dominant in the columns, which could inform behavior of the reactive CBZ and DCF.

To determine how much adsorption to soil media and how quickly CBZ/DCF may be degraded in the soils, soils from columns could be excavated after the experiment to quantify the mass of adsorbed PPCPs. If soils were rinsed in a controlled volume of a solvent like methanol, the adsorbed CBZ/DCF should remobilize into the liquid phase, where their concentrations could be determined in the HPLC.

7.2 Additional Areas of Study

Two primary areas were identified in this experiment as a direct continuation of this study: effects of the soil microbiome and effects of drying-wetting cycles.

As indicated in Section 2.3 Benefits and Applications of SAT there is an established connection between SOC and microbial activity in soils. This study along with the other reviewed studies all indicated that an increase in SOC corresponds to increased adsorption of target PPCPs. What has not been clearly identified however, is what role the soil microbiome plays in this relationship. Soil microbes present on soil surfaces may have an effect on rates and total adsorption of PPCPs in soils. They are also hypothesized to be a primary cause of the chemical reduction of complex organics into simpler monomers (Martínez-Hernández et al. 2016) in SAT, allowing not only for a removal of PPCPs from the liquid phase through adsorption, but also decreasing the bulk quantity of a target compound in the environment via biodegradation.

Such analysis would most likely require inoculation of soil in a new study with a known soil microbe or characterized microbial community, along with methods to analyze their populations and activity over the course of experiments. To measure the effective reduction or breakdown of target compounds, controlled abiotic experiments should be conducted in tandem with the microbially active experiments. Controlled masses of soil should then be removed from the columns post-experimentation and washed in a solution to desorb the CBZ/DCF from soil particles, and the resultant concentrations should be compared between the abiotic and microbially active soils.

A crucial factor in SAT efficiency is the management of drying/wetting cycles in soil which was not directly studied in the experiments conducted, but may have been indirectly observed in bench column experiments. After conducting the initial experiments, the top of each column was wrapped tightly in parafilm and the lower stopcock was closed. This was done so that more CBZ/DCF solution could be passed through the columns in the following days to extend breakthrough curves. Sealing each column was done in an attempt to maintain constant experimental conditions from the stopping point of one day's experiment, but upon continuing these experiments there was a sudden significant drop in outgoing concentrations for all columns (Figure 17).

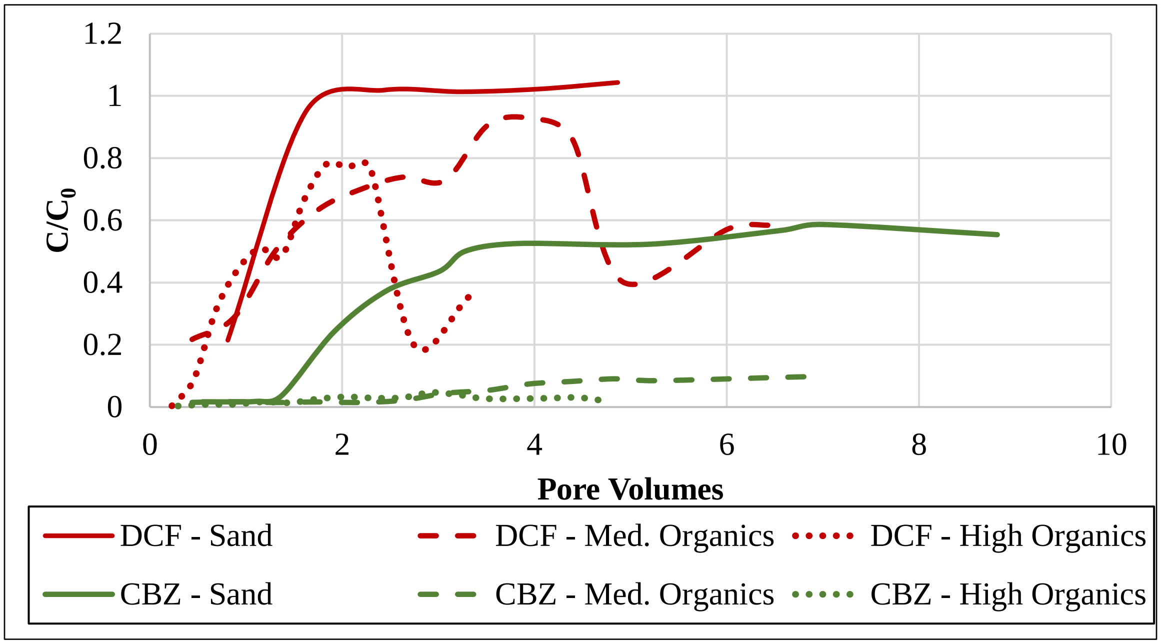


Figure 17: Drop in outgoing concentrations upon later resuming the experiment

This result may inadvertently suggest the effects of drying-wetting cycles in soils, but because this was not an intended goal of the study there is insufficient data here to make a conclusive statement.

Studies focusing on drying/wetting cycles (Silver et al. 2018) showed that removal of CBZ and DCF was greater in soils which were periodically wet then dried, than soils under constant infiltration. Bench and large-scale soil columns in this experiment were generally conducted under constant infiltration conditions, but when bench columns were unintentionally subjected to drying then rewetting, adsorption capacity appeared to increase. The role of drying/wetting cycles is hypothesized to be closely related to soil microbial effects mentioned above, where alternating aerobic and anaerobic conditions allow for different microbial communities to be active. Soils were not intentionally dried however, they were left at room temperature and sealed at the top, so evaporation and gravity drainage could only occur through the closed stopcock at column outlets. This clearly still affected the soils and adsorptive behavior, but was not an extensive drying cycle where soils were heated to 60°C in the open as done in (Seol and Lee 2001). It is also possible that the time before resuming the experiments was sufficient for any present soil microbiology to begin biodegradation of the adsorbed PPCPs because column soils were not sterilized. Whether PPCP degradation occurs through chemical or biological means, effects of drying and wetting are crucial to the understanding of SAT systems where PPCPs must be both adsorbed and degraded.

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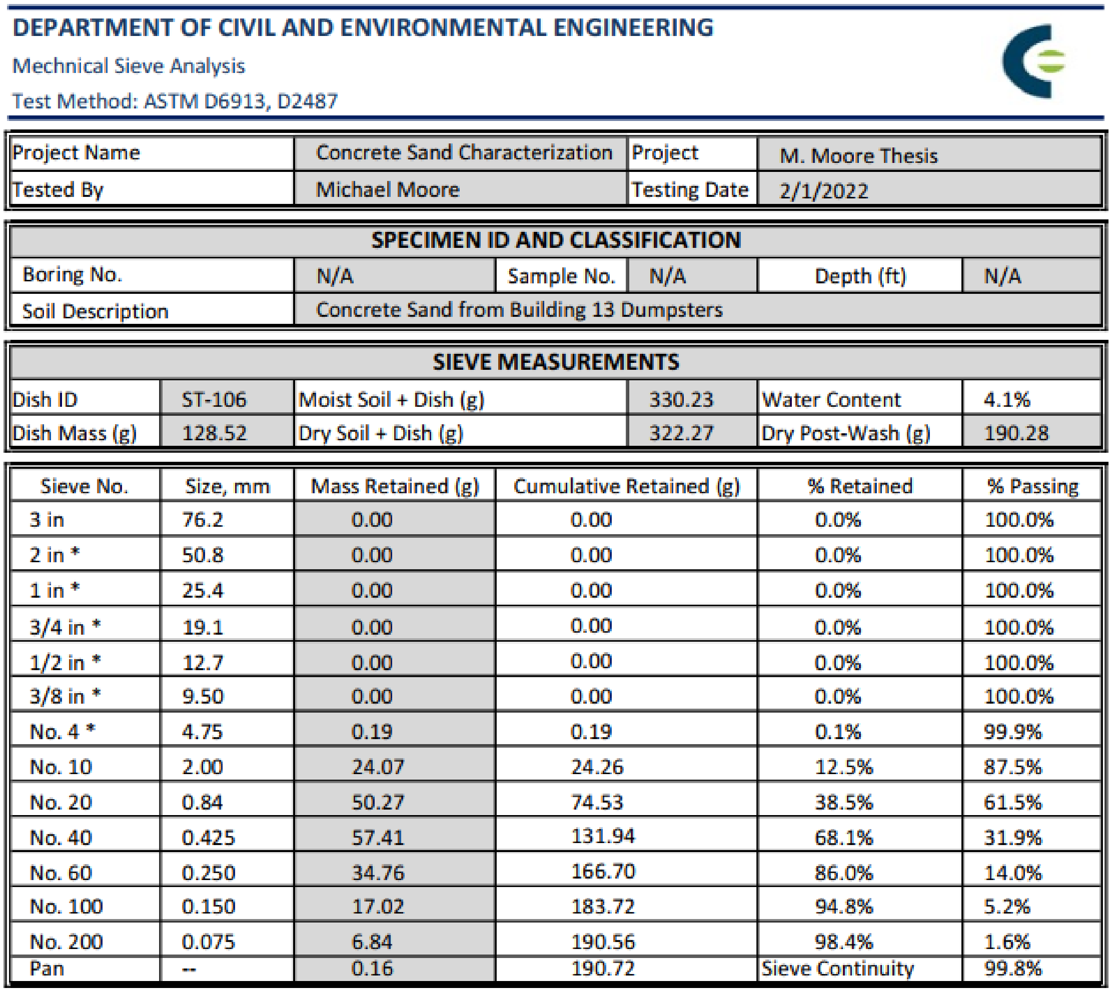
A. SOIL CHARACTERIZATIONS



DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

Mechnical Sieve Analysis

Test Method: ASTM D6913, D2487

Project Name	Concrete Sand Characterization	Project	M. Moore Thesis
Tested By	Michael Moore	Testing Date	2/1/2022

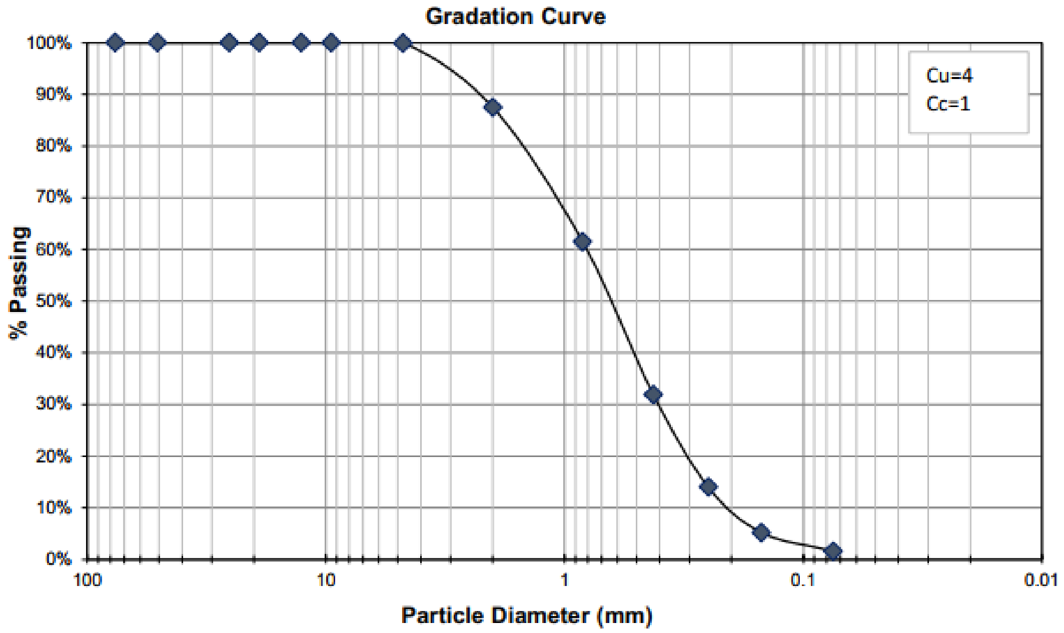
SPECIMEN ID AND CLASSIFICATION

Boring No.	N/A	Sample No.	N/A	Depth (ft)	N/A
Soil Description	Concrete Sand from Building 13 Dumpsters				

SIEVE MEASUREMENTS

Dish ID	ST-106	Moist Soil + Dish (g)	330.23	Water Content	4.1%
Dish Mass (g)	128.52	Dry Soil + Dish (g)	322.27	Dry Post-Wash (g)	190.28

Sieve No.	Size, mm	Mass Retained (g)	Cumulative Retained (g)	% Retained	% Passing
3 in	76.2	0.00	0.00	0.0%	100.0%
2 in *	50.8	0.00	0.00	0.0%	100.0%
1 in *	25.4	0.00	0.00	0.0%	100.0%
3/4 in *	19.1	0.00	0.00	0.0%	100.0%
1/2 in *	12.7	0.00	0.00	0.0%	100.0%
3/8 in *	9.50	0.00	0.00	0.0%	100.0%
No. 4 *	4.75	0.19	0.19	0.1%	99.9%
No. 10	2.00	24.07	24.26	12.5%	87.5%
No. 20	0.84	50.27	74.53	38.5%	61.5%
No. 40	0.425	57.41	131.94	68.1%	31.9%
No. 60	0.250	34.76	166.70	86.0%	14.0%
No. 100	0.150	17.02	183.72	94.8%	5.2%
No. 200	0.075	6.84	190.56	98.4%	1.6%
Pan	--	0.16	190.72	Sieve Continuity	99.8%



DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

Mechnical Sieve Analysis

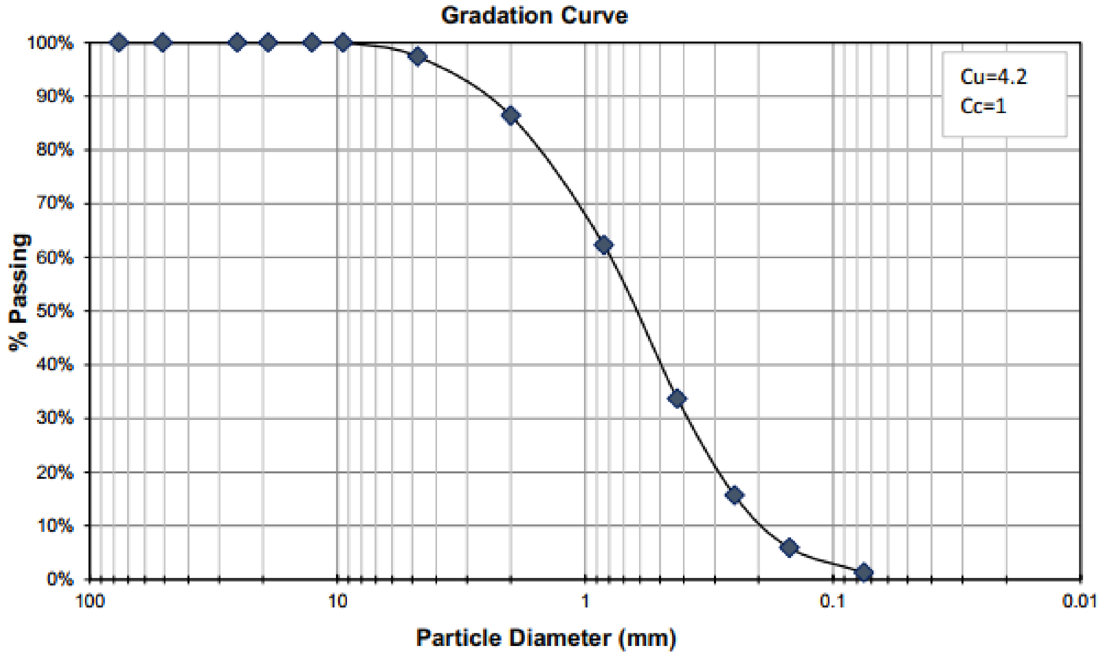
Test Method: ASTM D6913, D2487

Project Name	Organic Soil Characterization	Project	M. Moore Thesis
Tested By	Michael Moore	Testing Date	4/12/2022

SPECIMEN ID AND CLASSIFICATION					
Boring No.	N/A	Sample No.	N/A	Depth (ft)	N/A
Soil Description	Blend of 80% Concrete Sand 20% Topsoil				

SIEVE MEASUREMENTS					
Dish ID	ST-107	Moist Soil + Dish (g)	277.84	Water Content	13.0%
Dish Mass (g)	129.00	Dry Soil + Dish (g)	260.70	Dry Post-Wash (g)	131.70

Sieve No.	Size, mm	Mass Retained (g)	Cumulative Retained (g)	% Retained	% Passing
3 in	76.2	0.00	0.00	0.0%	100.0%
2 in *	50.8	0.00	0.00	0.0%	100.0%
1 in *	25.4	0.00	0.00	0.0%	100.0%
3/4 in *	19.1	0.00	0.00	0.0%	100.0%
1/2 in *	12.7	0.00	0.00	0.0%	100.0%
3/8 in *	9.50	0.00	0.00	0.0%	100.0%
No. 4 *	4.75	3.38	3.38	2.6%	97.4%
No. 10	2.00	14.57	17.95	13.6%	86.4%
No. 20	0.84	31.66	49.61	37.7%	62.3%
No. 40	0.425	37.67	87.28	66.3%	33.7%
No. 60	0.250	23.76	111.04	84.3%	15.7%
No. 100	0.150	12.94	123.98	94.1%	5.9%
No. 200	0.075	6.02	130.00	98.7%	1.3%
Pan	--	1.78	131.78	Sieve Continuity	99.9%



DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

Mechnical Sieve Analysis

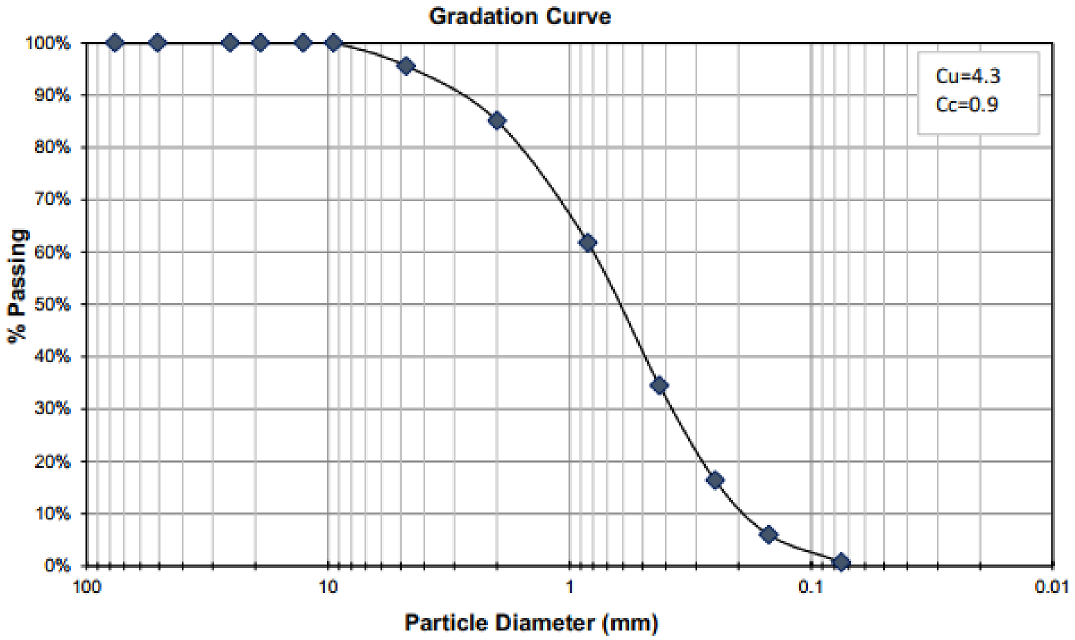
Test Method: ASTM D6913, D2487

Project Name	Organic Soil Characterization	Project	M. Moore Thesis
Tested By	Michael Moore	Testing Date	4/12/2022

SPECIMEN ID AND CLASSIFICATION					
Boring No.	N/A	Sample No.	N/A	Depth (ft)	N/A
Soil Description	Blend of 60% Concrete Sand 40% Topsoil				

SIEVE MEASUREMENTS					
Dish ID	ST-108	Moist Soil + Dish (g)	227.62	Water Content	24.2%
Dish Mass (g)	130.21	Dry Soil + Dish (g)	208.61	Dry Post-Wash (g)	78.40

Sieve No.	Size, mm	Mass Retained (g)	Cumulative Retained (g)	% Retained	% Passing
3 in	76.2	0.00	0.00	0.0%	100.0%
2 in *	50.8	0.00	0.00	0.0%	100.0%
1 in *	25.4	0.00	0.00	0.0%	100.0%
3/4 in *	19.1	0.00	0.00	0.0%	100.0%
1/2 in *	12.7	0.00	0.00	0.0%	100.0%
3/8 in *	9.50	0.00	0.00	0.0%	100.0%
No. 4 *	4.75	3.43	3.43	4.4%	95.6%
No. 10	2.00	8.23	11.66	14.9%	85.1%
No. 20	0.84	18.32	29.98	38.2%	61.8%
No. 40	0.425	21.40	51.38	65.5%	34.5%
No. 60	0.250	14.13	65.51	83.6%	16.4%
No. 100	0.150	8.17	73.68	94.0%	6.0%
No. 200	0.075	4.16	77.84	99.3%	0.7%
Pan	--	1.38	79.22	Sieve Continuity	99.0%



DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

Mechnical Sieve Analysis

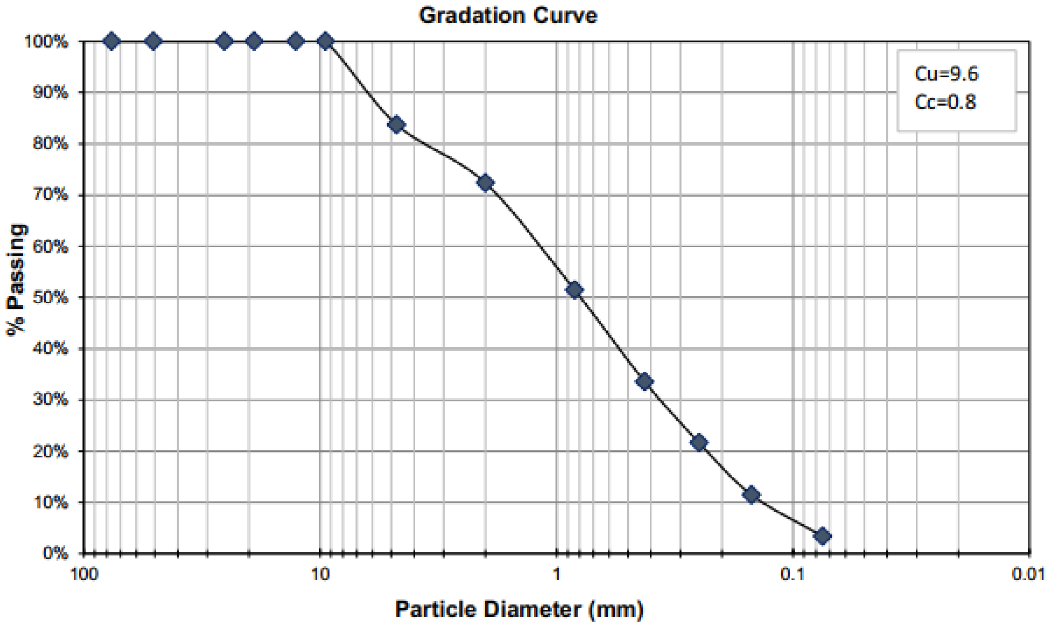
Test Method: ASTM D6913, D2487

Project Name	Organic Soil Characterization	Project	M. Moore Thesis
Tested By	Michael Moore	Testing Date	4/12/2022

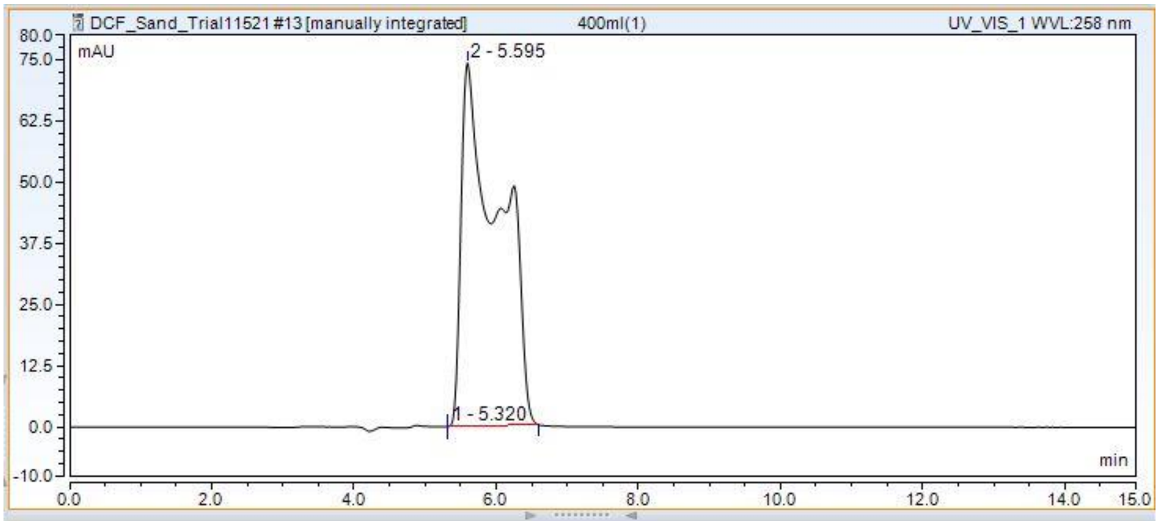
SPECIMEN ID AND CLASSIFICATION					
Boring No.	N/A	Sample No.	N/A	Depth (ft)	N/A
Soil Description	100% Topsoil without sand				

SIEVE MEASUREMENTS					
Dish ID	ST-112	Moist Soil + Dish (g)	227.01	Water Content	90.0%
Dish Mass (g)	130.10	Dry Soil + Dish (g)	181.11	Dry Post-Wash (g)	51.01

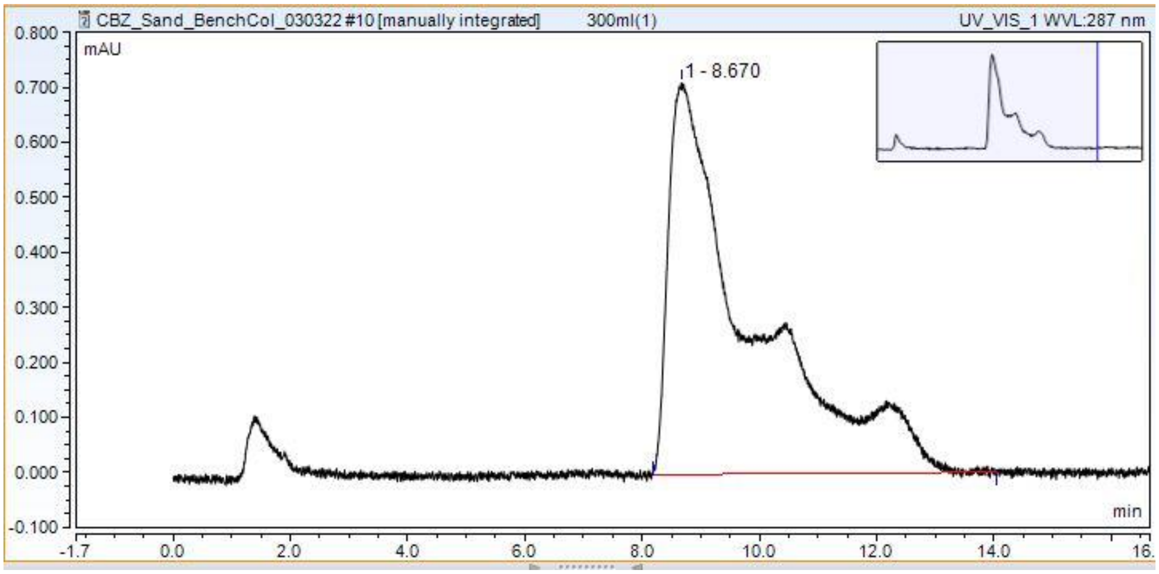
Sieve No.	Size, mm	Mass Retained (g)	Cumulative Retained (g)	% Retained	% Passing
3 in	76.2	0.00	0.00	0.0%	100.0%
2 in *	50.8	0.00	0.00	0.0%	100.0%
1 in *	25.4	0.00	0.00	0.0%	100.0%
3/4 in *	19.1	0.00	0.00	0.0%	100.0%
1/2 in *	12.7	0.00	0.00	0.0%	100.0%
3/8 in *	9.50	0.00	0.00	0.0%	100.0%
No. 4 *	4.75	8.28	8.28	16.2%	83.8%
No. 10	2.00	5.79	14.07	27.6%	72.4%
No. 20	0.84	10.69	24.76	48.5%	51.5%
No. 40	0.425	9.09	33.85	66.4%	33.6%
No. 60	0.250	6.09	39.94	78.3%	21.7%
No. 100	0.150	5.20	45.14	88.5%	11.5%
No. 200	0.075	4.15	49.29	96.6%	3.4%
Pan	--	2.07	51.36	Sieve Continuity	99.3%



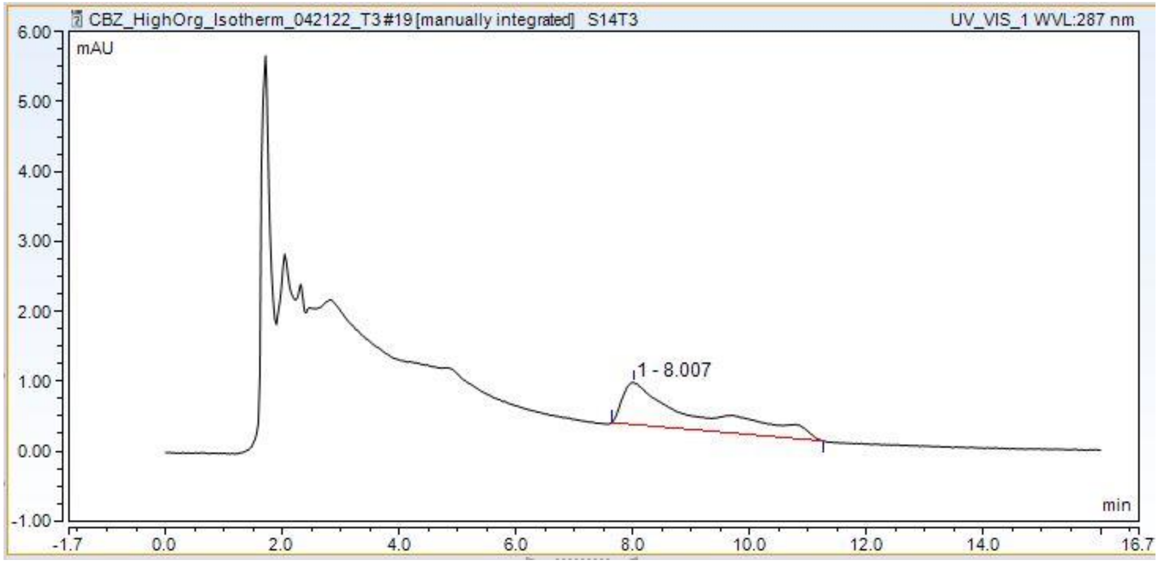
B. CHROMATOGRAPH INTERPRETATION



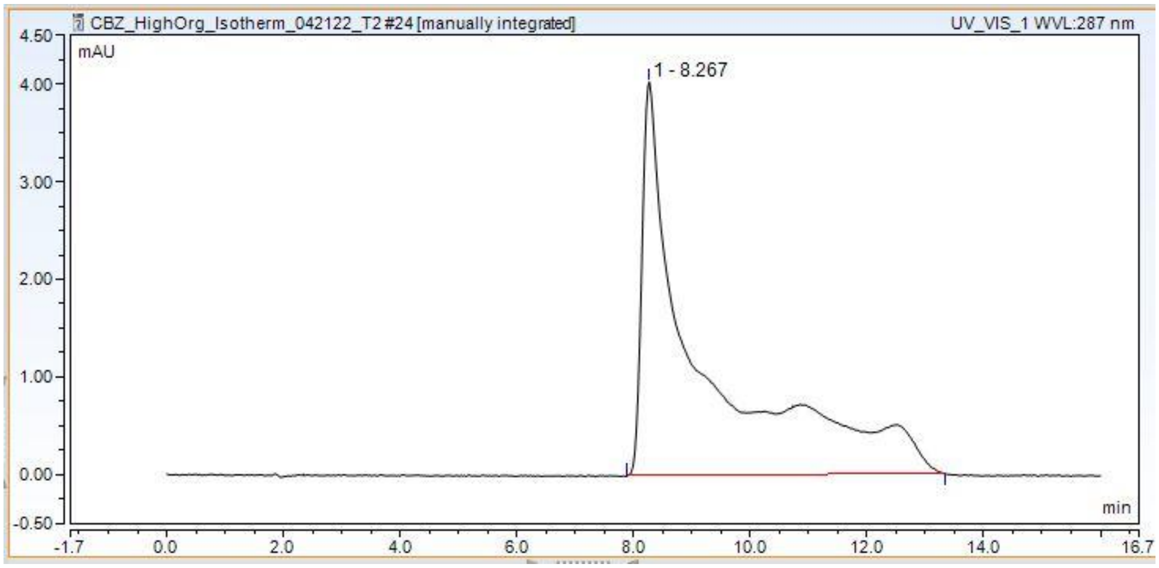
Example of a “clean” peak reading with no noise and strong signal (DCF-Sand)



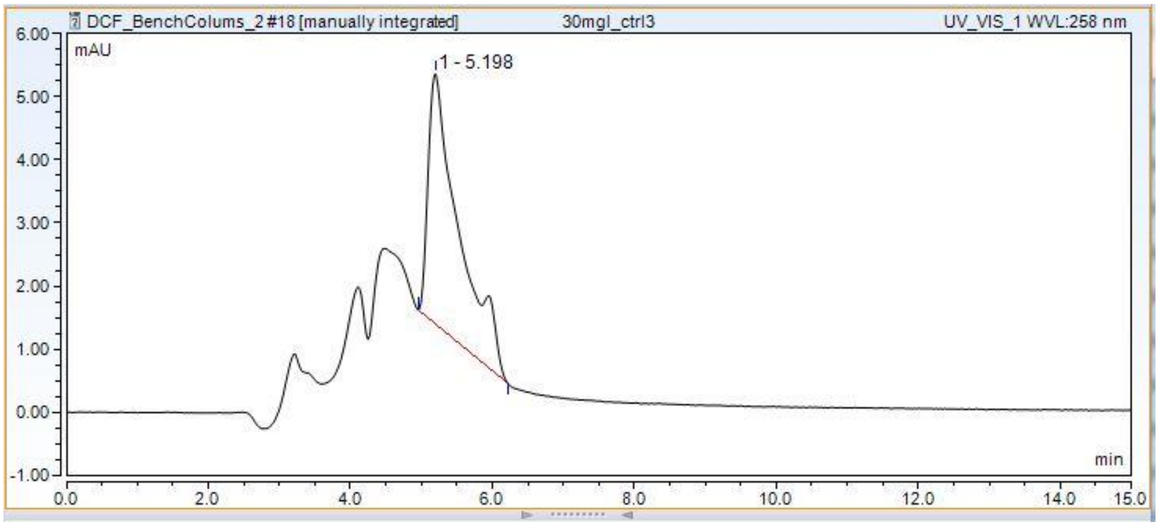
Example of a “shouldered” peak which is considered a single peak (CBZ-Sand)



Artificial peak in organic soil at ~1.5min, true peak beginning around 7.5min (CBZ-High Organic)

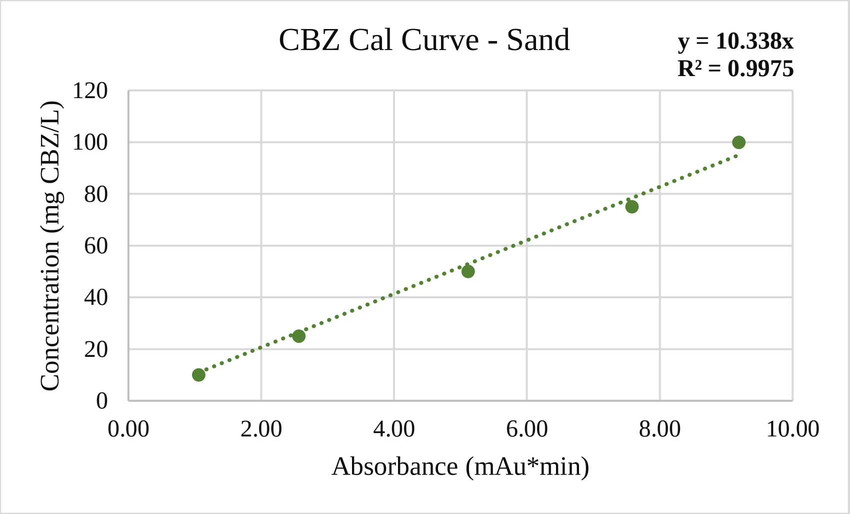


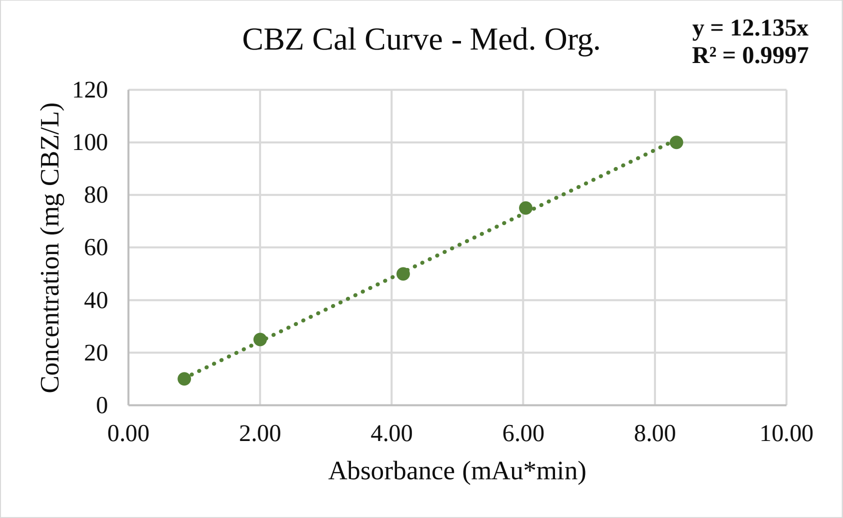
Using a "clean" peak from control data in the same experiment to confirm location of a true peak around 8min.

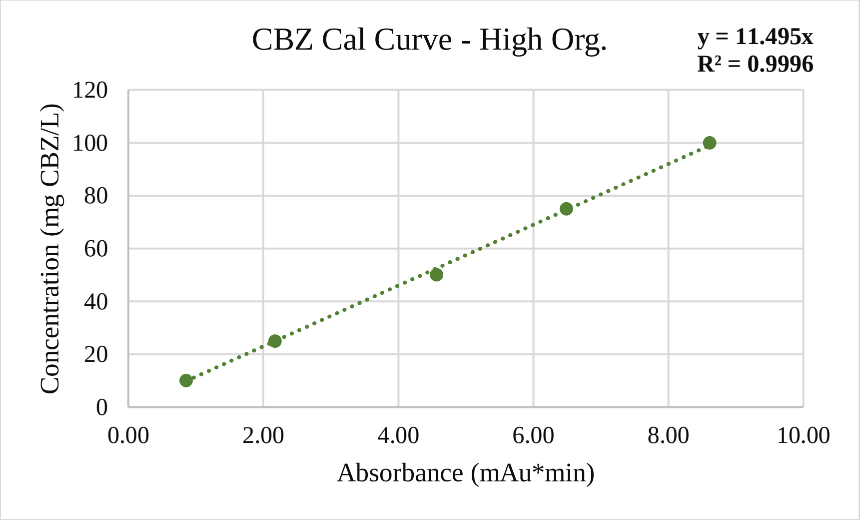


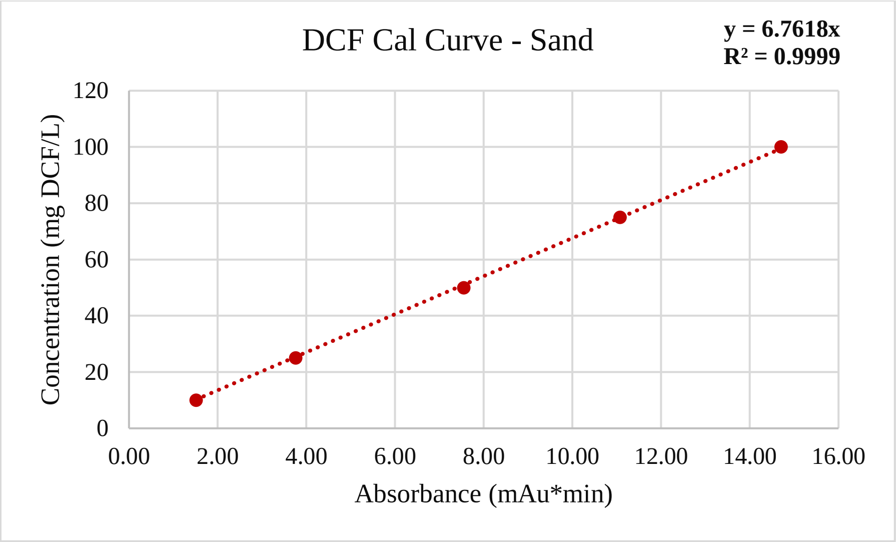
Process mentioned above to determine time of peak beginning and calibration curve values to determine peak area in more complicated signals.

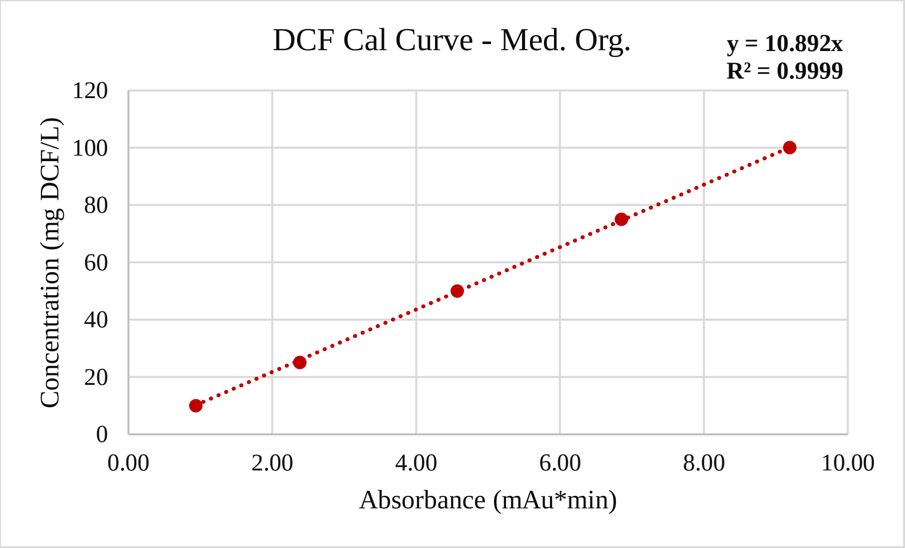
C. CALIBRATION CURVES

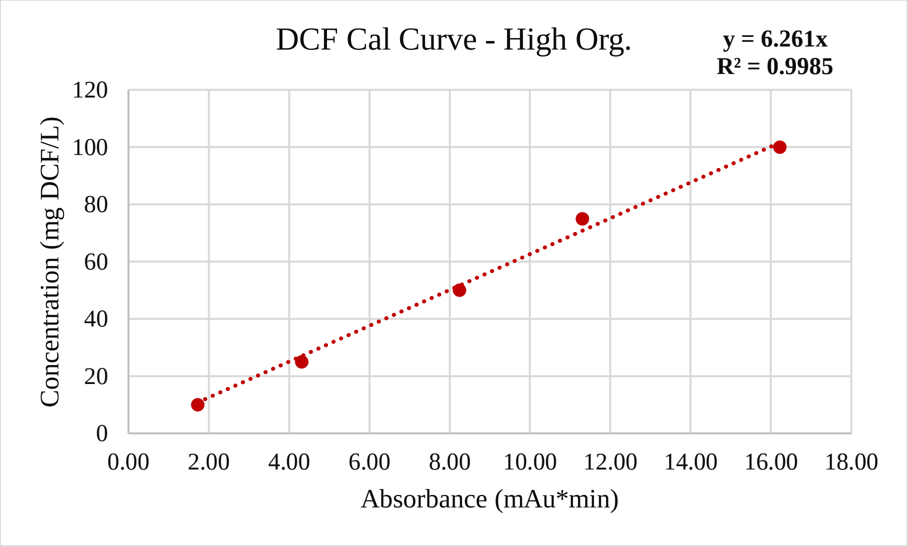




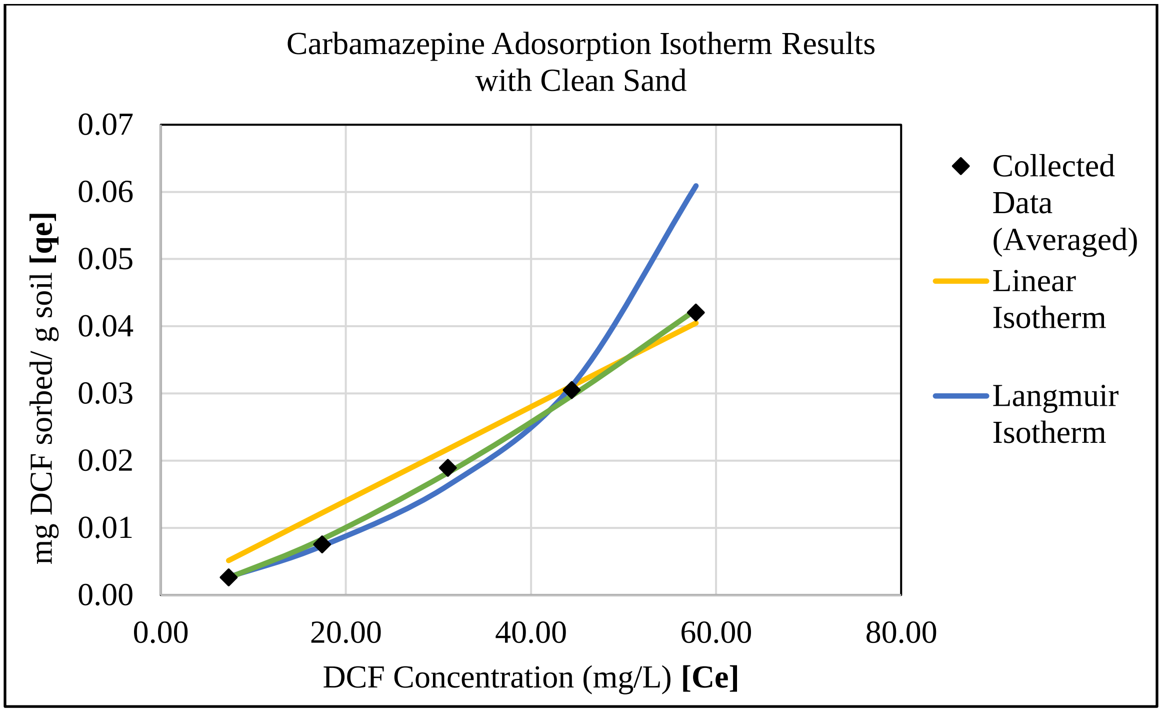


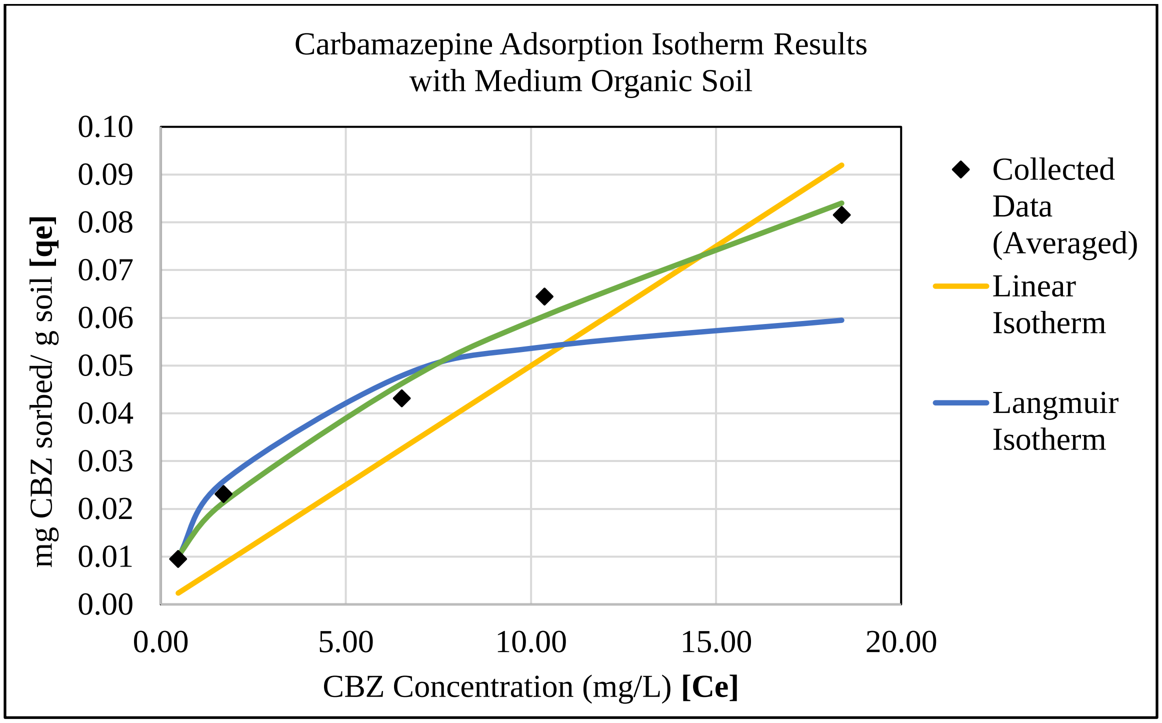

DCF Cal Curve - Sand
y = 6.7618x
R² = 0.9999
Concentration (mg DCF/L)
0
20
40
60
80
100
120
Absorbance (mAu*min)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00

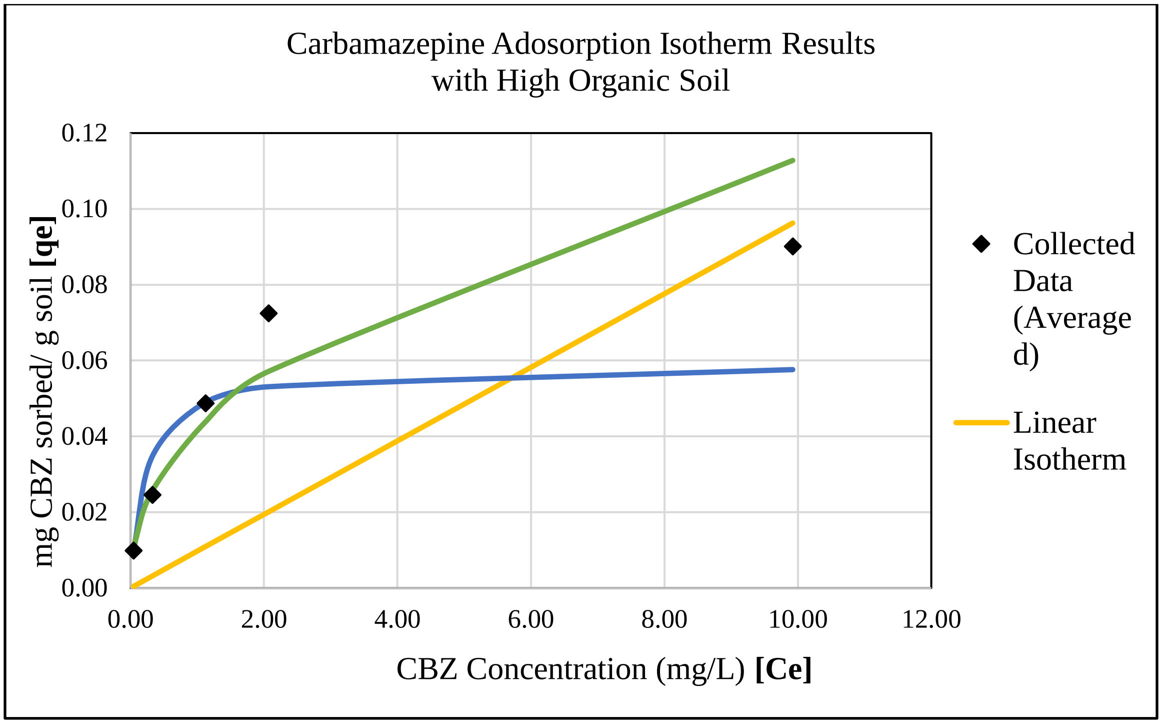

DCF Cal Curve - Med. Org.
y = 10.892x
R² = 0.9999
Concentration (mg DCF/L)
0
20
40
60
80
100
120
Absorbance (mAu*min)
0.00
2.00
4.00
6.00
8.00
10.00

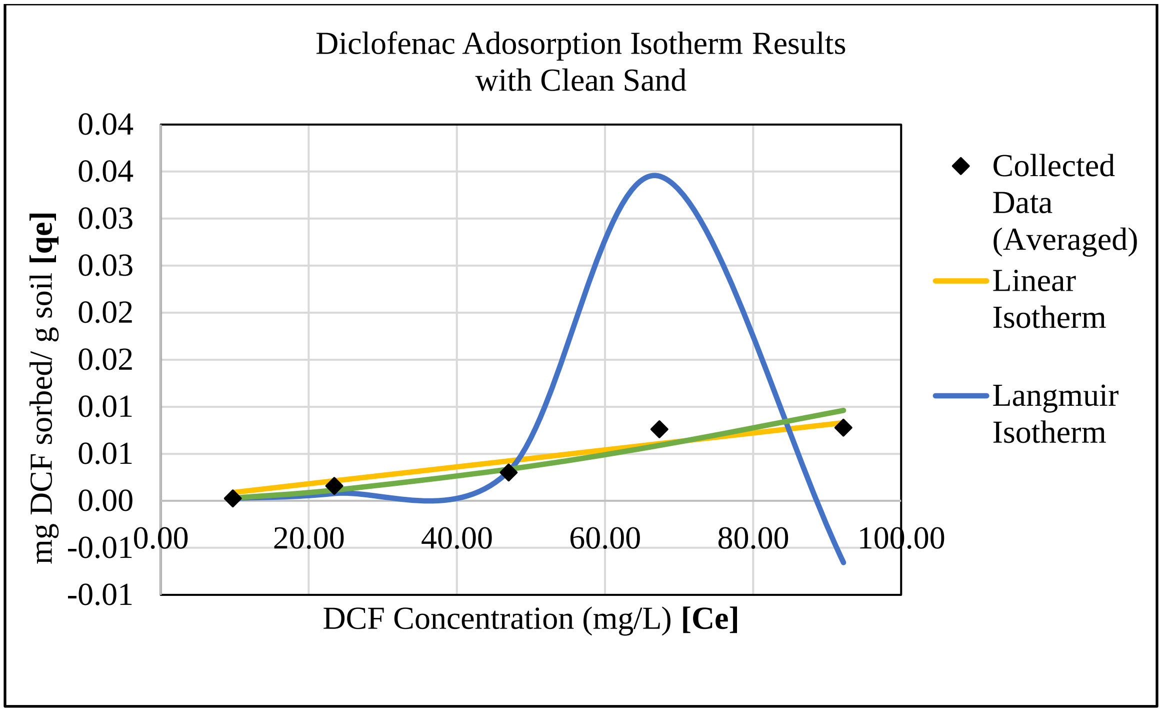

DCF Cal Curve - High Org.
y = 6.261x
R² = 0.9985
Concentration (mg DCF/L)
0
20
40
60
80
100
120
Absorbance (mAu*min)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00

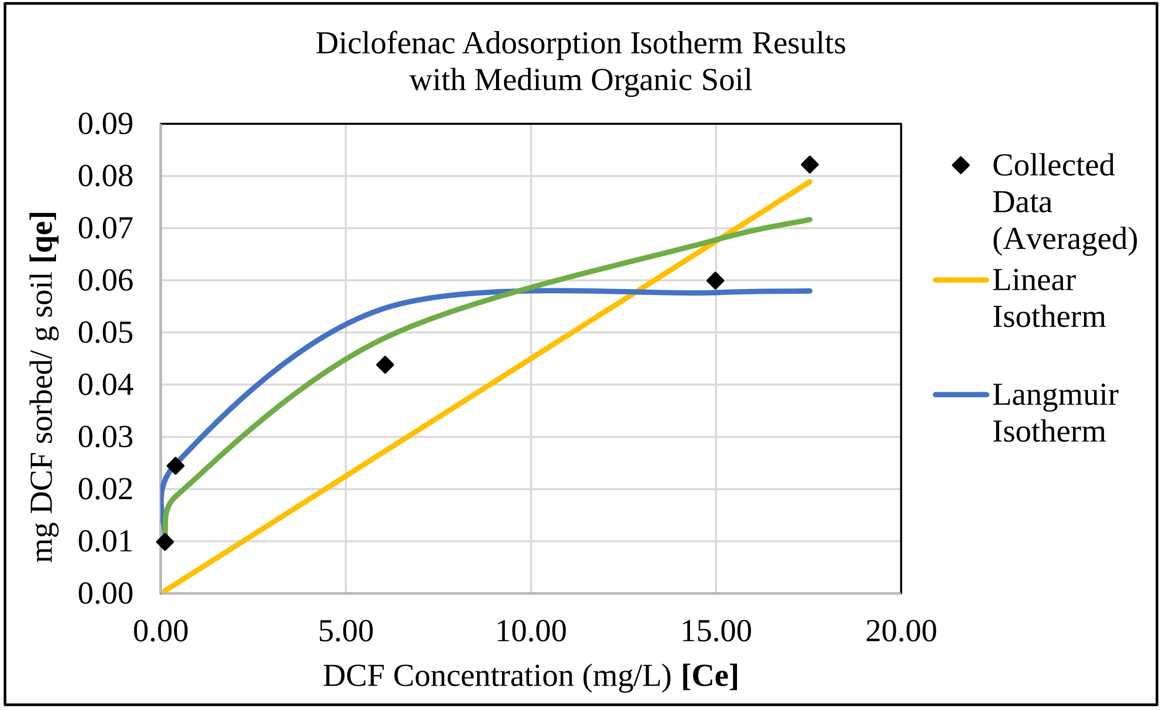
D. ISOTHERM MODEL FITS

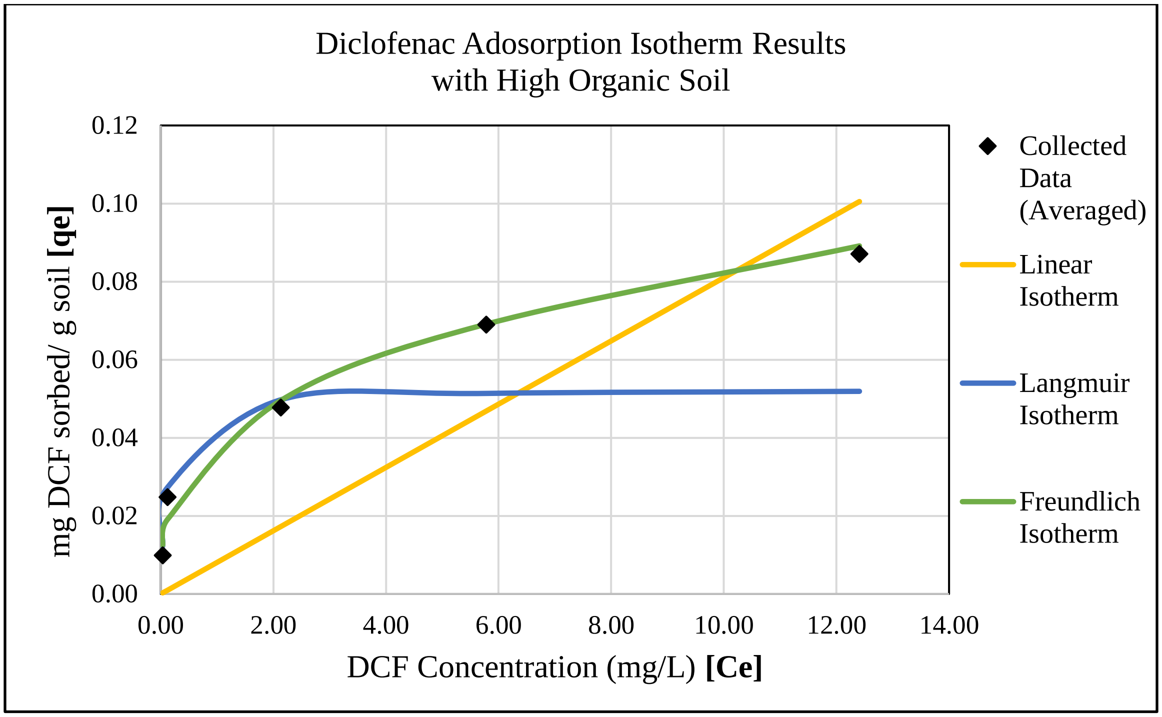





Carbamazepine Adosorption Isotherm Results
with High Organic Soil
mg CBZ sorbed/ g soil [qe]
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
CBZ Concentration (mg/L) [Ce]
◆ Collected Data (Averaged)
Linear Isotherm


Diclofenac Adosorption Isotherm Results
with Clean Sand
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
-0.01
-0.01
0.00
20.00
40.00
60.00
80.00
100.00
mg DCF sorbed/ g soil [qe]
DCF Concentration (mg/L) [Ce]
Collected Data (Averaged)
Linear Isotherm
Langmuir Isotherm


Diclofenac Adosorption Isotherm Results
with Medium Organic Soil
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0.00
5.00
10.00
15.00
20.00
mg DCF sorbed/ g soil [qe]
DCF Concentration (mg/L) [Ce]
Collected Data (Averaged)
Linear Isotherm
Langmuir Isotherm


Diclofenac Adosorption Isotherm Results
with High Organic Soil
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
mg DCF sorbed/ g soil **[qe]**
DCF Concentration (mg/L) **[Ce]**
◆ Collected Data (Averaged)
Linear Isotherm
Langmuir Isotherm
Freundlich Isotherm